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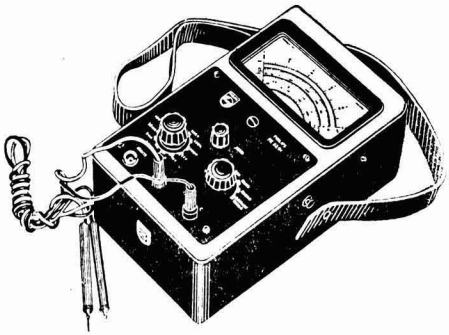

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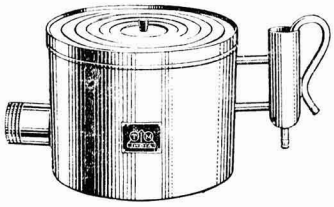

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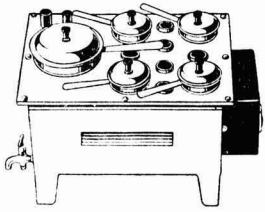

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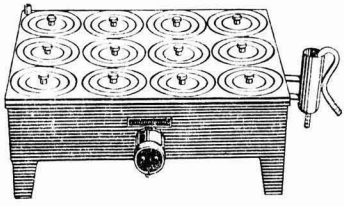

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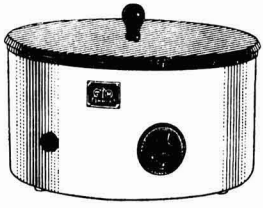

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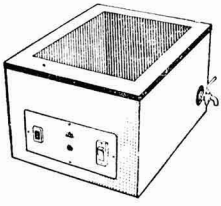

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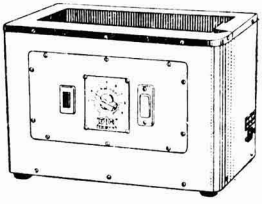

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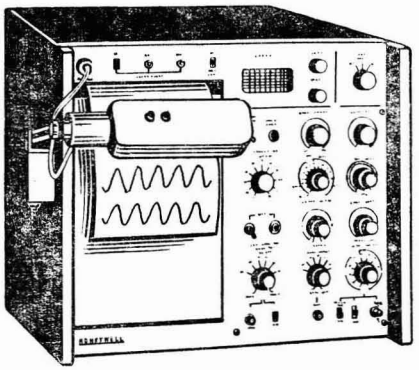

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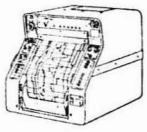

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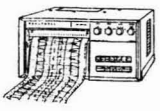

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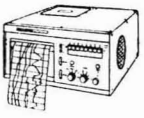

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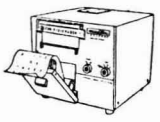

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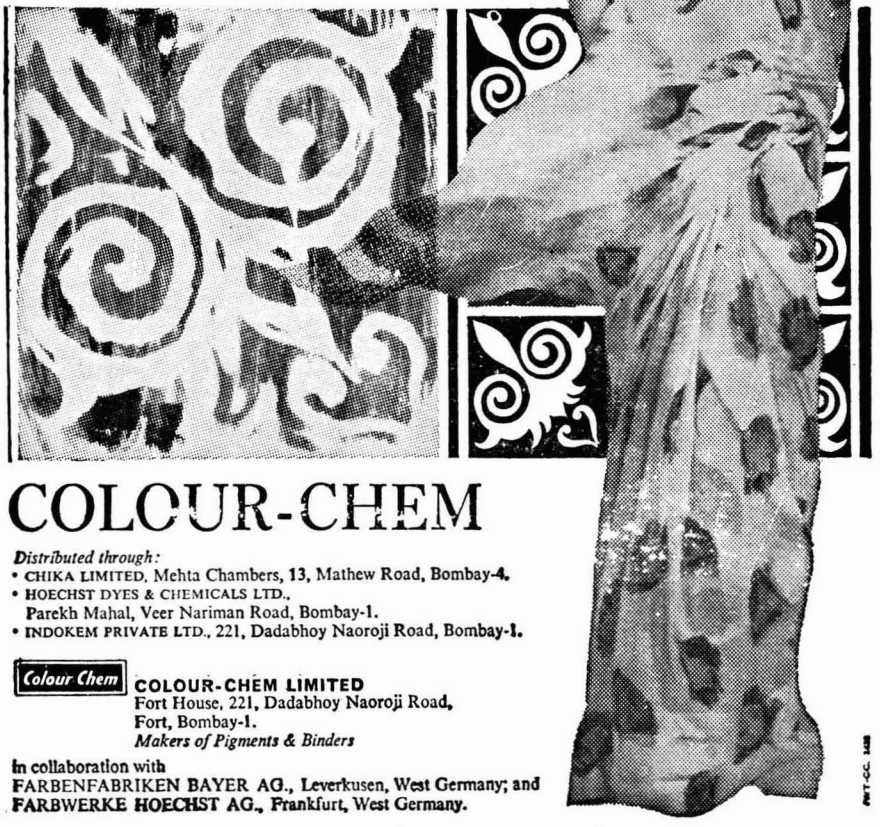

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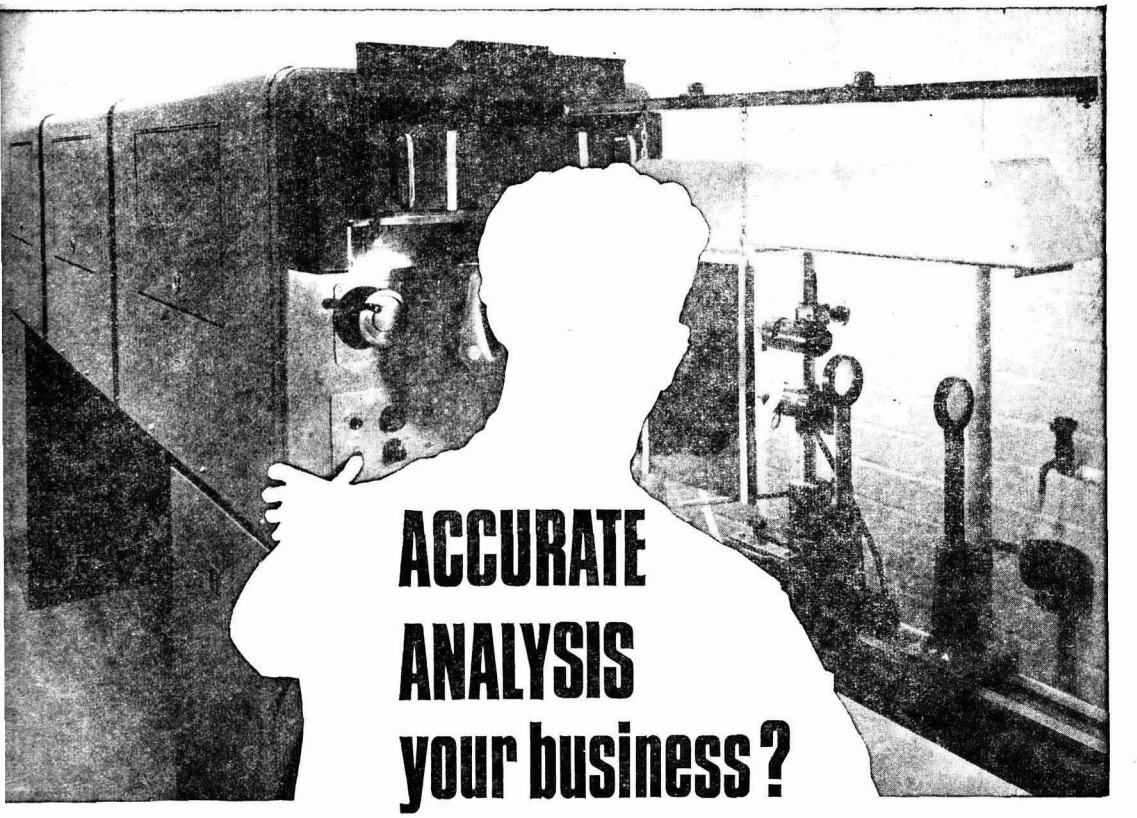

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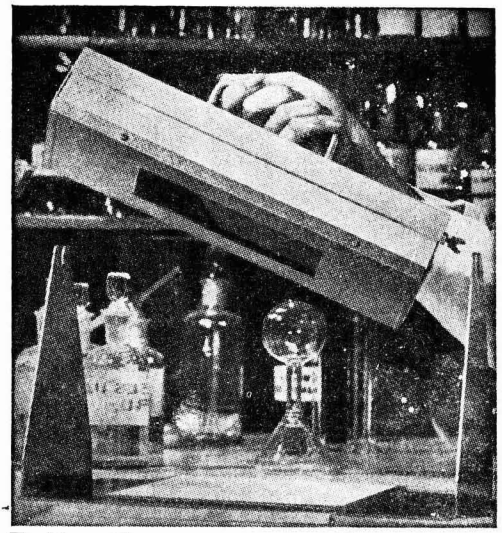

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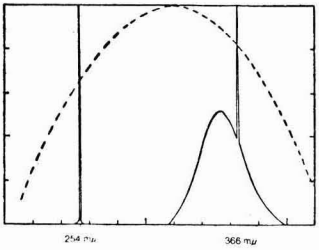

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Current Topics

Seminar on Man, Science & Society

AN interdisciplinary seminar, entitled 'Man, Science and Society', was organized by the Indian Institute of Advanced Study (IIAS), Simla, during 14-25 May 1968. Over fifty invited participants — scientists, artists, philosophers, sociologists, and men of letters and religion — took part in the seminar and presented papers. Dr Atma Ram, Director-General, Scientific & Industrial Research, inaugurated the seminar.

The seminar, ninth in the series organized by the Institute, was a departure from the earlier ones, and for the first time science and technology formed the central theme of discussion. It was rather intriguing why such a broad and complex theme was chosen, what particular reasons prompted the holding of the seminar and what special significance it had in relation to contemporary picture of Indian science and society. These questions were competently answered by Dr Niharranjan Ray, Director of the Institute, in his introductory address. The most important reason, according to Dr Ray, is that science and technology has brought about far-reaching changes in the structure of human society. It has also raised grave social, political and economic problems and tensions in all industrialized societies. Though India has not yet become an industrialized country, we have deeply committed ourselves to science and technology, and the problems and tensions afflicting industrially advanced nations today will plague India too. It is, therefore, imperative that India starts facing the situation, analyses and understands the problems science and technology will create and find answers for them. Thus, according to Dr Ray, the purpose of the seminar was to (i) underline the importance of the theme and the urgency for an understanding of its basic implications; (ii) gain an insight into the far-reaching effects of science and technology on contemporary and Indian society and take a look into the social organization of science in the country; and (iii) achieve an adequate understanding of the very complex problems of science and the social order in the context of the world situation, particularly the Indian one.

The broad scope of the seminar is indicated by the following titles of the sections into which it was divided: (i) Interaction of science and society; (ii) Science, politics, political ideologies and the state; (iii) Science, art, religion, philosophy and history; (iv) Science and human values; and (v) Sociology of science. The extremely broad canvas of the seminar and the large variety of topics covered were perhaps responsible for many of the papers and discussions being highly academic.

About a dozen papers dealt with problems of specific concern to Indian science and technology. In one paper, the author felt that while individual scientists in India are brilliant and effective, there have been no major self-sustaining scientific schools based on cooperative endeavour; the same causes lay behind the relative lack of vigour of professional societies. The author of another paper felt that scientists in India avoid facing crucial and important questions, and sufficient attention is not paid to problem raising, identification, selection and solution. Another author observed that the isolation and protection given to science in India prior to independence has made it an academic discipline, and it has not acquired the features of a social movement; one would have expected a radical change in the attitude of people to science after independence, but this has not happened. A third author deplored that in India political decisions taken on scientific and technical education have been to the detriment of the larger interests of the country. A participant observed that science in India continues to be object-oriented and the influence of this thinking is seen even in our planning, which is more related to materials instead of manpower. Another participant observed that India should think in terms of productive employment for the masses than of labour-saving devices, as Indian economy is labour intensive. Yet another participant pleaded for development research grants to industry for the manufacture of new items of equipment not manufactured in India.

To conclude, the seminar has in a way achieved its objective. It brought home how highly complex and closely interrelated are the problems one has to contend with while dealing with a vast theme like 'Man, Science and Society'. The seminar should help the IIAS to plan further seminars on more specific and narrower areas of the subject, with particular reference to India, so that a more coherent and clear picture of the role of science and technology and its implications in countries like India will emerge.

Dielectric Behaviour of Aqueous Electrolytic Solutions*

D. PREMASWARUP
Department of Physics, Andhra University Postgraduate Centre, Guntur

THE chief token by which an electrolyte is recognized, its electrical conductivity, was long ago traced to the transport of electrically charged matter. Salts, acids and bases possess this special kind of conductivity. The chief properties of electrolytic solutions are conductivity, osmotic pressure, depression of freezing point, elevation of boiling point, lowering of vapour pressure, dielectric constant, relaxation time, etc. Although it was since 1881 when Helmholtz[1] explained for the first time Faraday's laws of electrolysis on the basis of dissociation of molecules into anions and cations that attempts are being made to evolve a comprehensive theory of electrolytic solutions which can satisfactorily explain the observed properties, success is still unachieved. Theories and modifications, put forward from time to time, were unable to explain satisfactorily all the observed properties in the entire concentration range. The purpose of the present review is to describe briefly the various theories that were suggested, specially the more recent theories explaining the dielectric behaviour of solutions.

Earlier Theories

When it was realized that the simple application of thermodynamics to laws of solutions was insufficient to explain the observed properties of electrolyte solutions, namely osmotic pressure, depression of freezing point, elevation of boiling point, lowering of vapour pressure, etc., Arrhenius[2] suggested that only a fraction of the total number of molecules break up into ions in solutions. Since the electrical conductivity is a property which depends on the number of ions present in solution, the degree of dissociation can be determined from conductivity measurements as the ratio of the equivalent conductivity of the solution at any particular concentration to the equivalent conductivity at the limiting case of infinite dilution. While there is a general qualitative agreement to a first approximation between the degrees of dissociation thus calculated and those obtained from other observed properties like osmotic pressure, etc., small systematic differences, which could not be ascribed to experimental errors, are present, especially for strong electrolytes. These are arbitrarily attributed to the neglect of the interionic forces.

In contrast to the Arrhenius theory of incomplete dissociation, Lewis[3] proposed the use of an empirical parameter f_i, termed activity coefficient, which can be used to multiply the actual concentration γ_i to yield an apparent concentration $a_i = \gamma_i f_i$, which if used in place of γ_i yields correctly the observed properties from thermodynamical considerations on the basis of complete dissociation of all molecules at all concentrations. Support is given to this view by the optical behaviour of coloured electrolyte solutions where the intensity absorbed by a given amount of solute is in many cases independent of the concentration. Unless the undissociated molecules absorb in the same manner as the ions exactly, it must be assumed that the degree of dissociation is practically independent of the concentration. The variation of the activity coefficients are ascribed to the mutual interactions of the electrically charged ions. In successive modifications by Debye and Falkenhagen[4], Millner[5], Bjerrum[6], etc., two types of interactions are investigated: (i) the effect of a time averaged sheath of opposite charge termed the ionic atmosphere surrounding any charged particle in retarding the motion of the central ion, and (ii) the electrophoretic effect on account of which the ions have to move not through a stationary solvent but through a medium moving in the opposite direction.

Theoretical expressions based on these considerations[4-6] for the osmotic pressure, vapour pressure lowering, freezing point lowering, boiling point elevation, etc., agreed with experimental observations only at high dilutions (concentrations less than about 0·005). At higher concentrations the assumption made by Debye and Falkenhagen in treating the ions as point charges as compared to the thickness of the ionic atmosphere becomes more and more invalid and theoretical predictions disagree more and more from observed values with increasing concentrations. Modifications in the theory by Debye and Hückel[7], for the finite size of the ions, were not also very successful in explaining the observed properties at high concentrations. Bjerrum[6] put forward a theory wherein oppositely charged ions which are closer than a certain minimum distance are termed as associated and behave as a single particle. According to Bjerrum there can be 100 per cent ionization without 100 per cent dissociation and the ions associate together without any appreciable deformation of their electron orbits and without the formation of any more permanent chemical linkage. It is also possible for ion triplets to be formed. Other theories based on the concept of ionic association but differing in methods were also offered.

Nernst[8] revived the original Arrhenius theory of incomplete dissociation and tried to explain the observed heats of dilution and other properties by a theory including the effect of ionic interactions. His theory also was only partially successful. This concept of incomplete dissociation and generalized law of mass action including ionic effects was developed further by Onsager[9], Davis[10], McInnes[11], Fuoss and Krauss[12], etc.

*Paper presented at the convention organized by the Physical Research Committee of the Council of Scientific & Industrial Research at the Banaras Hindu University, Varanasi, in March 1967.

In contrast to the properties discussed above, which depend more or less on the long-range inter-ionic forces, dielectric properties depend on the interaction of the ions with the polar solvent molecules as related to the thermodynamics and kinetics of ions in solution.

Dielectric Behaviour

Experimental Results

Dielectric constants of aqueous solutions at moderate concentrations are very difficult to determine on account of their high conductivities and the resulting high values of the loss angle δ. At the frequencies available when the early measurements were carried out it was necessary either to work with extremely dilute solutions where the deviation from the dielectric properties of water are correspondingly small or to work with very high values of tan δ which greatly limited the accuracy of the measurement. It is even difficult from a study of the literature to ascertain whether the dielectric constant of an ionic solution increases or decreases with increasing concentration. However, with the development of microwave techniques the above limitations are removed as the conductivity loss decreases with increasing frequency. Some of the most important measurements of the real and imaginary dielectric constants for aqueous electrolytic solutions at microwave frequencies are by Hasted *et al.*[13], Haggis *et al.*[14] and Harris and O'Konski[15]. The experiments yielded the following results.

(i) There is in general a depression of the static dielectric constant. In dilute solution the dielectric constant ε_s decreases linearly with increasing concentrations, but at higher concentrations plots of ε_s versus concentration show considerable curvature with the slopes decreasing in absolute value at higher concentrations.

(ii) The limiting slopes δ at low concentrations of the solute are the same for a bromide or iodide as they are for the corresponding chloride. The slope for the fluorides is, however, larger than the slopes for the other halides. The cation slopes indicate that the dielectric constant depression decreases with increasing size among cations of the same charge, but this effect is not as large as that caused by changes in charge. The depression associated with the fluoride ion is considerably less than that associated with any of the cations studied. The general nature of the conclusions is not affected even if one takes into account the effect of the dilution of the water more rigorously.

(iii) The dielectric constant depression is greater at higher temperatures than at lower temperatures.

(iv) At low concentrations, the relaxation phenomena are characterized by a single Debye relaxation time which decreases linearly with concentration. The depression of the relaxation wavelength λ_s from the pure water value is dependent on the charge of the cation, increasing with increasing charge. It is also greater for the large ions than for smaller and much hydrated ions of the type Li^+, Mg^+ and H^+.

(v) As concentration increases, the depression of the relaxation times decreases and at still higher concentrations the relaxation times even become greater than the pure water value. Also at high concentrations there is a distribution of relaxation times as compared to the single relaxation time at dilute solutions.

(vi) The depression of relaxation time in dilute solutions decreases with increasing temperature.

Theoretical Interpretation

Dielectric constant—A qualitative explanation of the depression of the static dielectric constant is not too difficult. The electrolyte solution consists of the ions into which the solute molecules are dissociated, embedded in a medium consisting of the polar solvent molecules. On account of the very strong electric fields in the region immediately surrounding an ion, the solvent molecules surrounding the ion are more or less saturated, causing a lowering of the dielectric constant of the solution as a whole. A quantitative estimate of the effect is, however, more difficult as one has to take into account the radius of the ions, the strengths of the electric fields in the region surrounding the ions and the effect of these fields in changing the dielectric constant of the medium in the region surrounding the ions, factors about which present-day knowledge is very meagre. Hence a strict theoretical estimate is not possible and a number of approximations have to be made for even a reasonable qualitative estimate.

The earliest attempt in this direction was due to Sack[16], but as he used a Debye model for the dielectric constant of water, his calculated values came to be about a hundred times larger than the experimentally observed depressions. In a later calculation Hasted *et al.*[13] have used Onsager's[17] and Kirkwood's[18] models for a polar liquid to calculate the field strengths and hence the effective dielectric constants in the immediate neighbourhood of an ion. Their calculations show that within a distance of 2-4 A. the effective dielectric constant increases from a value of 4 to that of almost 80 and does not vary much at larger distances. Since below the distance of 4 A., which is of the order of the radius of the first hydration sheath, the representation of the dielectric as continuous will not be a valid approximation, the arbitrary simplifying assumptions are made that a positive ion can be represented as surrounded by a completely saturated first shell (of radius $r_+ + 2r_W$) and beyond that by a continuous dielectric of dielectric constant depending on the field strength, while a negative ion can be represented by a completely unsaturated first shell (of radius $r_- + 2r_W$) and dielectric constant ε_s, that of pure solvent surrounded by a continuous dielectric. Under these assumptions the dielectric constant decrements are calculated for positive and negative ions with radii 1 A. and the values obtained are $\delta^+ = -11{\cdot}5$; $\delta^- = -1{\cdot}5$ and $\delta^+ = -13$; $\delta^- = -3$ on Onsager's model and on a slightly modified Kirkwood's model respectively. These decrements are of the right order of magnitude. In view of the simplifying assumptions, an exact agreement beyond this is neither expected nor obtained.

A more quantitative estimation of the dielectric constant depression based on the same general principles is made by Glueckauff[19]. From the expressions derived by Booth[20] for the dependence of dielectric constant D on the field strength and the expressions for the field strengths in the neighbourhood of an ion derived by Debye and Hückel[21] one can write

$$D=n^2+(D_0-n^2)\frac{3}{u}\left(\frac{1}{\tanh u}-\frac{1}{u}\right)$$

where $u=\beta s$, s being given by

$$s=-\frac{\varepsilon z}{Dr^2} \text{ for } r<a$$

and

$$s=-\frac{\varepsilon z}{Dr^2}\left[\frac{e^{ka}(1+kr)}{(1+ka)e^{kr}}\right] \text{ for } r>a$$

with a representing the closest distance of approach. Solution of these equations gives D as a function of $rZ^{-1/2}$. In a first model, the continuous model, the dielectric constant D at any distance r is taken as having the value given by these equations. In an alternative model, termed the discontinuous model, the Booth equation is taken as obeyed only by the water outside the first water layer for monovalent ions and only outside the second water layer for multivalent ions. For the first and second water layers, constant values of $D=D_{w1}$ and D_{w2} corresponding to the values which are given by the Booth equation for the dielectric constants at the centres of these layers respectively are taken. Since the dielectric constant D is a function of the distance from the ion centre, each value of D is associated with a volume fraction

$$d\phi=2N'(4\pi r^2.dr)$$

where $N'=6{\cdot}05\times10^2$ C. is the number of electrolyte molecules per cc. and r is the radial distance from the centre. Taking $\phi=0$ when $r=0$ this gives $\phi=8/3.N'\pi r^3$, r having a maximum value r_x arising when $\phi=1$ with a given spatial distribution of local dielectric constant. The mean value of D of such a continuously non-uniform system can be obtained from the equation

$$\frac{dD}{d\log(1-\phi)}=\frac{3D(D\phi-D)}{2D+D\phi}$$

where $D\phi$ is the local value of D applying to the volume fraction between ϕ and $\phi+d\phi$.

When adding a disperse volume fraction $\phi_2-\phi_1$ of constant D $(=D_1)$ to a continuous volume fraction $(1-\phi_2)$ with $D=D_2$ the above equation gives for the mean value D of the mixture the integrated form

$$(\widetilde{D}-D_1)(D_2/\widetilde{D})^{1/3}=(D_2-D_1)(1-\phi_2)/(1-\phi_1)$$

and when the changes in D are small, i.e. when $(D_2-\widetilde{D})\ll D_2$, this simplifies to

$$D=D_2[2(D_2-D_1)(1-\phi_2)+3D_1(1-\phi_1)]/(3D_2(1-\phi_1)-(D_2-D_1)(1-\phi_2)$$

When using the integration equation, the integration must start at the point representing the continuous phase, i.e. in this case at $\phi=1$ and proceed towards the direction of incresing dispersion, i.e. towards $\phi=0$. The final value then is the required mean value $\widetilde{D}$. At each step the value of D given by the equations represents the mean value of D over the volume fraction treated so far. It is in the nature of the equation that the final result will be only slightly dependent on the exact dielectric constant of the ion itself because the volume fraction concerned is very small.

In dealing with a polyvalent electrolyte, the equations have to be modified slightly to take into account the different numbers of cations and anions present in the solution. One of the uncertain factors in the calculation is the value of β. Two alternative values, $\beta_1=0{\cdot}071/T$ as given by Booth[20] from theoretical considerations and $\beta_M=0{\cdot}116/T$ as given by Malsch[22] experimentally (but not necessarily accurate), are used in the calculations. Agreement of calculated and experimental values of dielectric constant depression for the fluorides, chlorides and iodides of Li, Na, K, Rb, Cs, Mg, Ba and La indicates that values calculated with β_1 are more accurate than those calculated with β_M. Although continuous and discontinuous models give similar results, the latter invariably gives values in better agreement with experimental results.

Recently, Krishna Mohana Rao and Premaswarup[23] extended Glueckauff's[19] calculations for more concentrated solutions and for different temperatures. The results at different temperatures showed good agreement with experimental values indicating the general validity of Glueckauff's method. At higher concentrations, however, the calculated results are always much lower than the experimental values. It is noticed that use of an effective ionic concentration αc instead of the actual concentration c (α being obtained from Λ_c/Λ_∞) brings the calculated results into much better agreement with observed values.

An attempt[24] was also made to apply the theory to solvents other than water by making calculations for solutions in methyl alcohol. But the value of β is not the same for water and methyl alcohol and the value for methyl alcohol was not available in literature. However, by trial and error a value of $\beta=0{\cdot}101/T$ was found to give good agreement between calculated and observed values of dielectric constants for different solutes.

Relaxation time — Relaxation times and depression of relaxation times in ionic solutions are more difficult to be interpreted in quantitative terms especially as the relaxation phenomenon in pure water itself is imperfectly known. There are two slightly different views for the qualitative explanation of the relaxation phenomenon. According to one, liquid water is considered as made up of ordered regions or microcrystalline domains whose boundaries are in continuous movements. When an electric field is applied, boundary movements result in orientations of water molecules in the field direction by replacement of empty lattice sites by molecules which themselves leave further spaces for replacement. Thus reorientation takes place at the moving boundaries of the broken pieces of lattice. Increasing temperature or inorganic ions in solutions are considered to break up the structure to some extent, to increase the boundary area

and shorten the relaxation time. An increase in structural temperature is shown also by the X-ray and spectroscopic data for ionic solutions.

Experimentally, Haggis *et al.*[14] have shown that solutions of organic molecules (like alcohols, phenols, ketones, etc.) have relaxation times longer than that of water. It is difficult to see how it is possible for these molecules to decrease the boundary area. Therefore, they developed a statistical approach in terms of the breaking up of the hydrogen bonds to supersede the structural concept. On this model pure water is regarded as having a broken down ice structure, a structure in which each molecule is striving to bond itself tetrahedrally to four neighbouring molecules just as in ice, but in which bonds are continually breaking and reforming. At any temperature T there are five types of water molecules present: four-bonded, three-bonded, two-bonded, one-bonded and zero-bonded. Four-bonded and three-bonded molecules form part of the structure and cannot become reoriented without breaking of bonds. Zero-bonded and one-bonded molecules can rotate without breaking a bond. Two-bonded molecules may also have to break a bond in order to rotate, but in the unsymmetrically bonded case the rotational energy barrier may be considerably lower than the energy of rupture. The increase in the dielectric constant of water ($\varepsilon=4$) over that of ice ($\varepsilon=3{\cdot}2$) in the far infrared region is attributed to the rotation of zero- and one-bonded molecules, whereas the increase from $\varepsilon=4$ to $\varepsilon=5{\cdot}5$ occurring in the microwave region is attributed to rotations of the unsymmetrically bonded two-bonded molecules. The bonded states will be in equilibrium with one another and the factor governing the reorientation of four- and three-bonded molecules will be the rate of formation, from these states of molecules, of the unsymmetrical two-bonded state which is assumed to rotate at higher frequencies than that at which they are formed. This rate will depend on the probability of breaking a bond $f_1(T)e^{-\Delta H/RT}$ and on the number of bond types from which this state can be formed, i.e.

$$\frac{1}{\tau}=(2m_{33}+m_{34}+m_{31}+m_{32})f_1(T)e^{-\Delta H/RT}$$
$$=2n_3f_1(T)e^{-\Delta H/RT}$$

This explains qualitatively the variation of the relaxation time of pure water with temperature. On this model the effect of ions or organic molecules on the relaxation time depends on whether the particles tend to increase or decrease the number of hydrogen bonds in solution. Positive or negative ions with water molecules bound to them by electrostatic forces cause a breakdown of hydrogen bonds and decrease the relaxation time while organic molecules which are linked to the water molecules by hydrogen bonding contribute to additional formation of hydrogen bonds and cause an increase in the relaxation times.

Conclusion

Qualitative explanation of the observed properties can be offered, sometimes from different hypotheses, but a rigorous theoretical calculation on the basis of any of these is not possible mostly because of the lack of knowledge of all the different factors involved. While the properties of very dilute solutions can more or less be satisfactorily explained, this is not so for even slightly concentrated solutions. Experimental work available in literature is mainly confined to salts of the first, second and third groups of elements. No data are available for salts of the transition group of elements. Work on these salts at concentration ranges from dilute solutions to high concentration may throw light on the state of the solutions. Again, use of liquids other than water as solvent, about which also the available experimental work is meagre, may yield some information about what happens when the salts are dissolved in different media. Collection of adequate experimental data in these directions may be necessary before any satisfactory attempt can be made to arrive at a model for the solutions which can successfully explain all the properties at various concentration ranges.

Summary

The earlier theories proposed to explain the observed properties of aqueous electrolytic solutions are briefly described. Although the original Arrhenius theory of incomplete dissociation is not generally accepted now, it is realized that due to association and formation of ion complexes, the effective number of ions in solution is less than the theoretical figure based on complete dissociation without association or complex formation.

Experimental results on dielectric constant and loss factors of aqueous electrolytic solutions show a lowering of these compared to the pure water values, the decrements increasing linearly with concentrations at low concentrations. The linearity is, however, disturbed with increasing concentrations. A model of the electrolytic solutions, in which the decrement of the dielectric constant is attributed to the strong electric fields in the neighbourhood of ions and the consequent lowering of the dielectric constant in these regions, satisfactorily explains quantitatively the observed results at low concentration. At higher concentrations, the decrease in the effective ionic concentration has also to be taken into account to bring calculated results into agreement with observed values.

Theoretical calculations of relaxation times are difficult and no completely satisfactory theory is available as yet. There is need for further experimental work especially on the salts of the transition group of elements, at low as well as high concentrations, before any successful comprehensive model explaining all the observed properties can be evolved.

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Some Observations on Turbulence in the Stratosphere over Minicoy Island*

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HIGH altitude supersonic transport is within sight now. Aircrafts would be cruising the stratosphere (60,000-70,000 ft) and for these flights special meteorological knowledge of the stratosphere would be needed. It is generally believed that in the stratosphere, where the temperature generally increases with height, the air flow is free from turbulences. It is shown in the present paper that F-type radiosonde observations indicate the existence of turbulence in the stratosphere up to heights of 20 km. (about 65,000 ft).

Turbulence in the Stratosphere

Prior to the introduction of radiosondes to determine the prevailing temperature and humidity in the upper air, Dines' meteorograph ascents made in India often showed that the end of the trace, where the balloon bursts in the stratosphere, is associated with a blur, indicating violent jerking oscillations. This jerk is noticed not only on the temperature trace but also on the humidity trace and in the datum pen at corresponding positions. Since all the pens are fixed to a frame which shifts with pressure, it appears that the blurs are associated with vibrations experienced by the aneroid. The only possible cause of such vibration appears to be the existence of turbulence in the stratosphere.

Sinha[1] examined the blur occurring in the records of Dines' meteorograph ascents at Agra and found that, in the 250 records examined, the blur occurred above 16 km. on 66 occasions and on 26 occasions they were above 20 km. Mani *et al.*[2] studied the Dines' meteorograph ascents in the Poona-Hyderabad and Madras-Bangalore regions. In the Poona-Hyderabad region, 126 flights were studied and of these 22 had blurs above a pressure of 100 m bars (16 km.). In the case of Madras-Bangalore, the corresponding figures were 180 and 79. Assuming that the pressure value of the displacement due to the blur indicates roughly the depth of the turbulent layer, it was observed that the mean thickness associated with all the blurs was about 1-2 km. and in the height region of 23 km.

Arnold[3] observed considerable turbulence in the stratosphere on four different occasions at Balmar, New Jersey, while tracking balloons with a telescope and radio-direction finder. The turbulence was so severe that the radiosonde separated from the balloon, though it was suspended by a cord with a nominal breaking strength of about 70 lb. During these observations in June 1950, the instrument separated from the balloon at heights ranging from 28 to 32 km. while in the observation in October, it separated at 24 km. He estimated that an ascending current of about 11 m./sec. could provide the necessary conditions for a free fall of the radiosonde of about 10 ft which could break the line.

Location of Turbulence Region in the Atmosphere from F-type Radiosonde Ascents

Venkiteshwaran and Jayarajan[4] have shown how observations of turbulence in the upper air can be made with the F-type radiosonde. Venkiteshwaran and Huddar[5] observed direct evidence of

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the existence of turbulence from the rate of rotation of the fan in the F-type radiosonde of the India Meteorological Department between 15 and 17 km., which represents the region just below the level of the lowest temperature in the tropopause. Evidence of turbulence from the rate of rotation of the fan was not available in the stratosphere since the flights then available did not extend into this region of the atmosphere. The general depth of turbulence regions below the tropopause was a bout 1-2 km.

Rate of Rotation of the Fan in F-type Radiosonde Ascent over Minicoy

The rate of rotation of the fan in the F-type radiosonde over Minicoy was studied for 41 flights during the period May 1963 to April 1964. Most of the flights reached the stratosphere, up to about 50 m bar. Fig. 1 shows the variations in the rate of rotation of the fan at different heights over Minicoy on 8.1.64 and 22.3.64. It can be observed from these soundings that severe turbulence was present in the tropopause extending into the stratosphere up to 50 m bar. It will also be observed that the bursting of the balloon and the termination of the flight was due to the turbulence experienced in the region. While this could only be inferred from the blurs at the end of the trace in the Dines' meteorograph[1], the radiosonde ascents over Minicoy bring out these facts clearly. It may be mentioned in this connection that the flights at Minicoy were all made late in the evening and, therefore, there was no solar radiation to affect the balloon fabric. Similarly, all the Dines' meteorograph ascents were made just after sunset. When soundings are made during the day, solar radiation warms up the balloon fabric appreciably and the hydrogen diffuses out at higher levels. The turbulence effects were not observed at higher levels in these flights.

Venkiteshwaran[6] described a simple method of estimating the vertical component of gusts in the upper air from the F-type radiosonde records. This referred to instances when the rate of ascent of the balloon was constant. The rate of rotation of the fan in these cases decreased gradually and steadily with height, due to the decrease in the density of the air.

However, it is observed from the Minicoy ascents that the rate of rotation of the fan remains unchanged with height up to as much as even 150 m bar (Fig. 1), and there were some instances in which it even slightly increased at the higher levels. This can be due only to the increase in the rate of ascent of the balloon with height[7].

Estimation of Vertical Component of Gusts in the Stratosphere over Miaicoy

Since the rate of rotation at Minicoy remains unchanged up to about 150 m bar and since it cannot be so unless the rate of ascent also increases with height, it is assumed that the increase in the rate of ascent of the balloon maintains the rate of rotation of the fan unchanged.

If we examine the flight at Minicoy on 8.1.64 (Fig. 1) for an initial rate of ascent of the SR 875

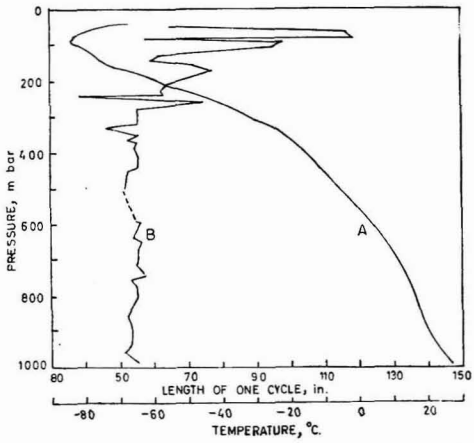

Fig. 1 — Variations in the rate of rotation of the fan and temperature at different heights (expressed in terms of pressure) over Minicoy on 8.1.64 and 22.3.64 [A, temperature; B, rate of rotation; and - - -, data not available]

balloon of 22 km./hr, the rate of ascent at 10 km. will be approximately 25 km./hr, and at 20 km. it will be 34 km./hr for the prevailing conditions of pressure and temperature. The rates of ascent of balloon in different ranges of height were 22·5, 26·0, 26·0 and 23·5 km. when computed from the time taken by the balloon to reach 5, 10, 15 and above 15 km. respectively. The maximum height reached by the balloon was 21·7 km.

Associated with the increase in the rate of ascent, the rate of rotation of the fan remained unchanged up to 10 km. (300 m bars), but above this level the rate of rotation decreases due to the rate of ascent of the balloon not increasing further and even falling at heights above 15 km. But the turbulence at 20 km. caused the rate of rotation of the fan to approach the value at 10 km. If it is assumed that the rate of ascent of the balloon continued to increase even above 10 km., it would have been about 34 km./hr at 20 km. and as a result the rate of rotation of the fan could have been the same as at 10 km. But the actual average rate of ascent above 15 km. was only about 23·5 km./hr. It may, therefore, be roughly estimated that on 8.1.64 the vertical component of the gust in the stratosphere was about 10 km./hr.

Thickness of the Turbulent Region in the Stratosphere

It is observed from Fig. 1 that there is turbulence in the tropopause extending up to 20 km. (50 m bars) At this height, the balloon fabric will have a thickness of only about 0·014 mm. and it has apparently burst due to the turbulence. Since the turbulence starts in the region of about 100 m bar and is observed up to 50 m bar where the balloon bursts, the thickness of this region is at least 4 km. An examination of 41 ascents over Minicoy during 1963-64 indicated that this type of turbulence is

prevalent in the stratosphere particularly in the winter months (January-March). However, in the monsoon months (June-September), it is more predominant in the lower regions, between 250 and 100 m bar, and the turbulence above the 100 m bar level is not as intense as in the winter months.

Conclusion

The F-type radiosonde ascents clearly prove the existence of regions of turbulence even in the stratosphere and it is shown how the value of the vertical component of the gust associated with this turbulence can be estimated. It is presumed that this new line of investigation will be of great value to supersonic transport.

Summary

From a number of F-type radiosonde flights, extending up to 20 km. (65,000 ft) over Minicoy Island during 1963-64, the variations in the rate of rotation of the fan in these radiosondes are examined. This analysis shows that the rate of rotation remains unaltered up to about 150 m bar, decreasing thereafter. It is shown that this is due to the rate of ascent of the balloon increasing up to this height and remaining steady or even decreasing at higher altitudes. It is observed from these flights that turbulence occurred in the region 45,000-65,000 ft, particularly during the months of January-March. A method of estimating the vertical component of the gusts in the stratosphere from these records is described. It is observed that the thickness of the turbulent region is more than 15,000 ft above the 50,000 ft level. These observations of turbulence in the stratosphere confirm the inference drawn from the blur in the Dines' meteorograph records.

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Silicone Resins in Cellulose, Glass, Ceramic & Allied Industries

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THE applications of silicone resins in surface coating industry, with special reference to silicone varnishes, lacquers and paints were reviewed earlier[1]. The present article reviews the recent developments in the use of silicone resins in cellulose, leather, glass and ceramic industries, and masonry and structural works. The status of simple organosilicon compounds *vis-à-vis* structurally complicated polymers, particularly their method of preparation and application in the above industries, is also considered.

Textile Industry

Earlier workers[2-5] have indicated the importance of silicones in textile industry, where water-proofing of textile fabrics is an important consideration. Silicones have been found to be highly effective in imparting water-proofing property to textile materials, such as steelon, porous artificial silk, etc.[6]. Natural and synthetic textile materials are made water repellent by coating them with silicone resins and curing at room temperature using N,N′-diphenylguanidine as a catalyst[7].

Cellulose fabrics have been made water repellent by the use of cyclic derivatives of organosilicon compounds, prepared by heating alkoxysilyldiamine with urea, with or without solvent[8].

An aqueous solution of pyridinium salt obtained by the reaction of alkylchlorosilane and pyridine is used for water-proofing animal and vegetable fibres[9]. Quaternary ammonium derivatives of silicon compounds have been reported to improve the water repellency, softness, dimensional stability, flame resistance and crease resistance of textile materials[10].

Gilkey[11] has reported the preparation of water-soluble organosilicon-chromium Werner coordination compounds; he recommended their use for water-proofing textiles.

Rayon yarn when treated with tetracetyloxysilane $[Si(OC_{16}H_{33})_4]$ or dicetyloxydiethoxysilane $[(C_{16}H_{33}O)_2 \cdot Si(OEt)_2]$ showed high heat resistance. The latter, even in low concentration, increased the dry and wet strength of yarn[12].

A mixture of polyvinylsilane and methylsilicone is polymerized in the presence of peroxide catalyst in an inert solvent and the mixture coated on the textile fibres to give water repellent and stain resistant finishes[13]. A silicone made by the simultaneous polymerization of tetravinylsilane[14] and methyl hydrogen siloxane with benzoyl peroxide as catalyst and methyl isobutyl ketone as solvent is an excellent water repellent for cotton fabrics. Crease proofing resins can be incorporated in the formulation.

A water repellent composition for cotton, rayon, nylon, etc., is obtained by emulsifying a cohydrolysed product of dimethyldichlorosilane and lauryltrichlorosilane and compounding the emulsion with aqueous solution of melamine-formaldehyde resin and zinc acetate[15].

Marshall and Cooper[16] reported a water repellent silicone formulation for textile fabrics based on copolymers of dimethyldiethoxysilane, γ-aminopropylmethylethylsilane and trimethylethoxysilane. Fabrics treated with this formulation showed high water repellency even after subjecting them to extraction with benzene.

Silicon esters[17] have been used for imparting slip resistance to fibres. When textile fibres are immersed in an aqueous emulsion of silicon ester and then dried, a film of hydrated silica is deposited on the fibrous surface, which increases its roughness and slip resistance. These fibres can be rendered water repellent by treatment with a liquid silicone or by exposure to dimethyldichlorosilane, with subsequent hydrolysis.

Fabrics treated with methyl hydrogen polysiloxane need curing at 150° to acquire water repellent property. If lead naphthenate is added, water repellency can be obtained by ageing the treated fabric at room temperature. According to Nakao and Wada[18], the treatment causes oxidation of the Si-H bond as well as the formation of intermolecular crosslinking of methyl hydrogen siloxane. By using stannous octoate, stannous oleate or stannous naphthenate as catalyst, lesser amounts of siloxane are required to obtain textile finishes with high degree of resistance. Stannous oleate and stannous naphthenate have 4-5 times higher bath life than stannous octoate. The preparation of catalysts and the siloxanes used for textile finishes has been described by Solomon and Ashby[19].

Cotton, wool, rayon, satin and terylene are water-proofed by treating them with methyl hydrogen polysiloxane and butyl titanate[20]. Textiles have also been rendered water repellent by the use of a mixture of methyl polysiloxane, urea-aldehyde or melamine-aldehyde resin with salts of titanium, zirconium, tin, lead, aluminium, zinc or nickel as catalysts[21].

When cloth or fibre is treated with a solution of polymethylhydrosiloxane and zinc acetate[22] or zinc octoate, good water repellent properties are imparted to it. $Al(OEt)_3$ is also used in place of zinc acetate for the same purpose[23].

An emulsion of methyl hydrogen polysiloxane-cetyldimethylbenzyl ammonium chloride-zinc acetate[24] has been used to impart water repellent finish to cotton clothes. Silicone emulsions[25] are also used for impregnating fabrics and silicone oils for oiling threads and yarn.

The relationship between resin structure and the properties imparted to the fabric has been discussed by Fortess[26]. Silicone finishes on apparel fabrics enhance their general performance and overcome specific shortcomings for special end uses. Silicone resins based on liquid methyl siloxane

polymers containing reactive groups for subsequent crosslinking on the fabric have been found to impart durable water repellency, resistance to aqueous borne stains, increased tear strength and abrasion resistance and improved sewability and recovery from wrinkling.

Crosslinking of methylhydro-, dimethyl- and methylamyl silicones with different peroxides[27] has been reported to give water repellent finishes surrounding the individual fibres, leaving open interspaces between the fibres for the passage of air. Improved crease resistance and wash-wear properties are also imparted to the cotton without loss of tear strength. The efficiency of the process varies with the molecular weight of the silicone, the peroxide used and the curing temperature. Phenyl substituted silicones do not produce these effects.

Wool can be made non-felting[28] by building a film of silicone polymer on the fibre surface to mask the scales responsible for shrinkage. Shrinkage of wool[29] is also prevented by treating the fabric with a benzene solution of mono- and diorganosiloxanes with a setting catalyst until 0·5-5 per cent of the mixture has been absorbed, followed by curing at 100-300°F. Specific examples of monoorganosiloxanes used in the above formulations are vinyl, allyl, octadecyl and phenylsiloxanes and those of diorganosiloxanes are dimethyl, diethyl, ethyl methyl, methyl butyl, methyl propyl, vinyl methyl, allyl ethyl, phenyl methyl and phenyl ethyl siloxanes.

Nylon can be made impermeable and hydrophobic by treatment with a composition[30] comprising linear polydimethylsiloxane containing terminal Si-OH groups, poly(methyl hydrogen siloxane), 7-amino-5-aza-1-sila-1,1,1,trimethoxyheptane and dibutyltindilaurate. Compositions containing linear poly-(dimethylsiloxane), poly(methyl hydrogen siloxane), and resins such as acrylate resin, urethane resin or chlorosulphonated polyethylene have also been employed for the above purpose.

Silicones have been used in textile machines. A typical example is the prevention of the formation of nylon gel on metal parts of fibre spinning equipment[17,31] by coating these parts with silicone liquid or solid.

Paper Industry

Silicones find extensive use in the manufacture of water repellent and 'adhesive' papers[32]. Even simple organosilicon compounds[33] have been used in the hydrophobization of papers, the most effective materials being the mixture of tetraacetoxysilane and dimethyldiacetoxysilane, the mixture of tetraacetoxysilane and diethyldiacetoxysilane, and the reaction product of silicon tetrachloride and trimethylchlorosilane with acetic anhydride. A 5 per cent solution of tetraacetoxysilane also gives satisfactory results. The mechanical properties of filter, wrapping and kraft papers are not affected by this treatment. A catalytic amount of tetraethoxytitanate reduces the drying time.

Paper can be rendered water repellent by the use of a mixture of methyl polysiloxane, urea-aldehyde or melamine-aldehyde resin together with a metal salt as catalyst[23].

Treatment with an aqueous solution of the alkaline hydrolysis products of an organotrihalosilane[34] (e.g. butyltrichlorosilane), either before or after sheet formation, improves the wet strength and sizing properties of paper. A subsequent treatment with aluminium sulphate reduces the curing temperature.

Sensitized flame-proof copy sheets used in the thermographic reproduction process are prepared by incorporating organosilicon compounds in the base sheet[35]. Impregnating papers with silicones and alkyl titanates[36] prevents the adherence of sticky materials; the impregnated papers can be used for wrapping purposes.

Siloxane resin[37] prepared from α,ω-dihydroxypoly(phenylmethylsiloxane), and polymethylsiloxane with di-*n*-amylpropaneboronate, is used for coating the papers to impart water repellency. α,ω-Dihydroxypoly(phenylmethylsiloxane) is prepared by the polymerization of a mixture of octamethylcyclotetrasiloxane and octaphenylcyclotetrasiloxane in the presence of a very small amount of potassium hydroxide. The poly(methylsiloxane) resin is obtained by cohydrolysis of methyltrichlorosilane and dimethyldichlorosilane. An emulsion prepared from poly(methylsiloxane) in toluene and zinc acetate solution has been used for coating the papers. These coated papers can be used for wrapping photographic films[38].

A composition[39] comprising dimethyl polysiloxane (mol. wt, 350,000-550,000), methyltriacetoxysilane and dibutyltindilaurate is applied to paper; curing at room temperature imparts non-adhesive properties to the paper. Contact with these papers does not impair the adhesion of adhesive tapes. If dimethyl polysiloxane of low molecular weight is used, the adhesion of the tapes to wrapping is impaired, since silicone resin tends to migrate to the surface of the paper. Hot tar can be filled in containers made of paper treated with the above silicone composition; after cooling, tar can be removed from the containers without difficulty. These papers can be used for making containers for food, especially pastry, and such foodstuffs as are to be heated.

Leather Industry

Different types of organosilicon compounds have been used in leather industry to impart water repellency, and to improve tear and wear strength and the hygienic properties of leather. Chelates[40] obtained by the treatment of β-diketones or β-keto esters with reactive zirconium compounds when incorporated in silanes and applied to leather surfaces imparted them satisfactory water repellency. Water-soluble organosilicon-chromium Werner coordination[11] compounds have also been used for water-proofing leather. Polymonocamphylsiloxane and polymonocyclohexylsiloxanes[41], when dissolved in an organic solvent and applied to leather, impart water repellency to it.

The elasticity of leather is increased when organosilicon compounds like tetraethoxysilane or phenyltricresoxysilane[42] are incorporated in cellulose based lacquers that are used to fix acrylic coatings on leather.

Maminov and Voronkov[43] and Maminov[44] investigated the suitability of several organosilicon compounds for water-proofing leather and found $MeSi(OCOMe)_2$-$OCOC_{17}H_{35}$, $EtSi(OH)_2ONa$ and $MeSiH(OMe)_2$ to be satisfactory as water-proofing agents for leather. The former was applied in toluene solution, whereas the latter two were used in aqueous solutions. These three compounds not only impart good water resistance, but also increase the hygienic properties of the treated leathers. The tensile strength as well as the other wear and tear properties of the leathers were also improved.

Glass Industry

Glass surfaces are made water repellent by applying an emulsion of ethylphenylsiloxane[45] in carbon tetrachloride with a small amount of hydrofluoric acid added. The chemical stability[46] of glass can also be increased by coating its surface with organosilicon compounds. To increase the resistance of glass to the action of organic liquids, the surface is first treated with a solution of silicic acid ester and later with heterosiloxane containing phosphor; the glass is then tempered at 80-120°C. Similarly, glass bottles and glassware are protected from minor abrasion and scratches by coating with a composition containing a siloxane[47,48], such as tristearate trisiloxane amine hydrochloride. No heat treatment is needed to cure this type of coating; it also does not show creeping tendency.

Weather resistant coatings on plate glass[49] are obtained by first exposing them in a chamber to an atmosphere of 80 per cent relative humidity and then coating with vapours of methyl trichlorosilane containing a small amount of methyl chloride. Chlorinated organosilicon compounds have also been used for treating glass surfaces to make them water repellent[50].

Flawless organosilicon coatings are obtained on glass vessels by applying emulsions based on isopropyl and ethyl alcohol solution of silicone resins and aqueous triethanol amine oleate[51].

Silicone resins are used for protecting the soft glass outer envelopes of high pressure mercury vapour lamps from corrosive atmospheres, especially when they are operated in an atmosphere of sulphur dioxide[52]. The silicone used for coating the lamps should be light transmitting and substantially transparent in thin layers. A coating composition based on silicone resin when applied to lamps makes them shatter proof and gives glass a permanent decorative finish[53].

Organosilicon compounds, such as trialkyl and triarylfluorosilanes[54], have been used in plasticized resin compositions for coating safety glass for improved stability against colour development and decomposition.

Useful properties are imparted to glass fibres by coating them with an adhesive and lubricating liquid composition based on a hydrolysable monoalkylsilane[55,56] with 10-31 carbon atoms; compounds of the type $C_{12}H_{25}SiCl_3$ or $C_{18}H_{37}SiCl_3$ are used in toluene solution in the above composition.

Water-proof finishes on glass fibres or fabric for improving the adhesion of the resin to glass in plastic laminates are obtained by treatment with vinyltrichlorosilane[57]. The reaction mixture is filtered and neutralized with hydrochloric acid to *p*H 4. Clean glass cloth is then immersed in the solution for a second and cured. Polyester laminates treated with this silicone exhibit a wet strength of 50,000 lb./in. as against a value of 25,000 lb./in. for untreated laminates. The glass fabrics are made soft and crease resistant[58] by first subjecting them to an oxidizing atmosphere below their fusion temperature. They are then coated with silicone fluid or polysiloxane to impart the desired properties.

A chemical finish on glass fibres[59] or other siliceous materials used in reinforcing plastics is obtained by treatment with a solution containing equimolecular quantities of allyltrichlorosilane and phenols. Organosilicon compounds, such as allylphenoxydichlorosilane, allyl-*m*-tolyloxydichlorosilane, allyl 3,5-xylyloxydichlorosilane and allyl (*m*-methoxyphenoxy)-dichlorosilane are also used in the above formulation.

Organosilicon compounds like methacryloyloxypropylsilane, epoxysilane, and bis-hydroxyethylaminopropylsilane[60] have been used for obtaining finishes on glass cloth used in laminate compositions. Methacryloyloxypropylsilane is very effective in polyester systems. Epoxysilane is ideally suited for polyesters, epoxy, phenolic and melamine resins, the last compound being recommended mainly for epoxies. Improved bonding between epoxy resins and glass is obtained by curing various silicone forming solutions on the glass fibres at 250-350°F. for a few minutes, prior to treatment with the epoxy resins[61]. The silicone primers[61] used are 3-triethoxysilyl phthalic anhydride, trichlorosilylacetic acid, trimethoxysilylpropionamide, etc.

Glass fabrics finished with a combination of vinyltrichlorosilane[62] and β-chloroallyl alcohol give laminates with satisfactory physical properties. Soluble salts of vinylsiloxanols are very good finishing agents and can be applied in aqueous media.

Glass fibres and fabrics when coated with water-soluble potassium isobutyl or sodium amylpolysiloxanolate acquire antistatic properties[63].

A composition imparting high water resistance and superior mechanical properties to glass surfaces, such as glass fabric polyester laminates, is prepared by dissolving a mixture of organosilicon compounds, such as methyltrichlorosilane, vinyl trichlorosilane and dimethyl dichlorosilane, in benzene-ethyl acetate solvent, treating the mixture with ethyl alcohol, and then with water; the oily product obtained is taken up in toluene and refluxed with boric acid and then applied to the glass surface[64].

Spitze and Richards[65] investigated the properties of glass surfaces treated with different silicones. They observed that methyl and phenyl groups in the silicone molecule impart maximum heat resistance to the glass surfaces and the dodecyl and octadecyl groups in the silicone molecule furnish maximum water repellency. Raolecki and Pickos[66] reported that compounds of the type tetrapropoxysilane, tetraisopropoxysilane and isopropoxypolysiloxane exhibit the best hydrophobic properties. It was also observed by these workers that the films formed by esters with branched chain are more

resistant to hydrolysis than those formed by esters with straight chain[66].

A variety of organosilicon films applied to glass surfaces were investigated by Hyde *et al.*[67]. They found that the contact angle with water, surface resistivity, and dry lubricity of the treated surfaces were invariably higher than those for untreated glass.

Ceramic Industry

Several organosilicon halides, ethers and polymers find extensive use as water-proofing agents in the ceramic industry. Damp ceramic material surfaces[68] are treated with ethyltrichlorosilane, diethyldichlorosilane or alkyl or arylorthosilicates to impart water repellency. These organosilicon compounds get hydrolysed on damp surfaces and during curing at elevated temperatures undergo crosslinking, forming films which contribute to water repellency. Ethylorthosilicate[69] also works as a ceramic binder.

Water repellent coatings on porous ceramic materials[70] have been obtained by aqueous hydrolysis of a mixture of *sec.*-amyltrichlorosilane, phenyltrichlorosilane, silicon tetrachloride and butyl acetate under controlled conditions to give siloxanol which is polymerized by heating under reduced pressure. A similar formulation is obtained by processing as above a mixture of [1-(dichlorophenyl)ethyl]-trichlorosilane, ethyltrichlorosilane, silicochloroform and butylacetate.

Stain resistant coatings for ceramic materials[71] are obtained by heating a mixture of γ-aminopropyltriethyoxysilane, phenyltriethoxysilane and diglycidylether of bisphenol A.

An air drying coating composition of silicone resins suitable for ceramic surfaces has been obtained by treating partially hydrolysed alkoxysilane with linseed fatty acid followed by glycerol phthalate[72].

Masonry and Building Structures

Sodium methylsiliconate solution is used for imparting water repellency to masonry bricks, pavements, etc.[73]. It is obtained by hydrolysing methyltrichlorosilane; the water insoluble methylsiliconic acid obtained is then treated with aqueous sodium hydroxide solution. Sodium methylsiliconate is also found to be a much more effective water repellent for different types of limestones than methylsilicone resin[74].

Polyorganosiloxanols[75,76] obtained by hydrolysing a mixture of methyl, ethyl, butyl and phenyl chlorosilanes are applied as solutions in organic solvents like toluene, xylene, white spirit, acetone, etc., to the surfaces of bricks, concrete, wood, etc., to give more superior water-proofing properties. The resin solutions can be stabilized with either borax or pyridine and can be stored for several months.

Water-soluble (organosilicon compounds are also used as water-proofing agents[77]. They are prepared by reacting ethylene glycol with an alkylalkoxysilane in the presence of an acidic catalyst. A 4 per cent solution of this resin is used for water-proofing materials like asbestos shingles, masonry, etc.

A 5 per cent kerosene solution of methyltrichlorosilane was found effective as a protective coating for white-washed walls[78]. The hydrophobic properties of this coating after 4 years of exposure remained unaffected, while on the control side of the untreated walls, even the original white-wash did not last. Similarly, the walls of the buildings when covered with 2 per cent aqueous solution of sodium methyl siliconate[78,79] were effectively protected. Approximately 1 lb. of the 2 per cent solution is required for every 20 sq. ft of the wall surface.

The hydrolysis product of a mixture of butyl[80] or ethyl[81] trichlorosilane and silicon tetrachloride has been used for application on masonry work. *n*-Hexadecylsilane and di-*n*-hexadecylsilane are also used as water-proofing agents for masonry[82]. Likewise, aqueous solutions of ethyltrimethoxysilane and methyltriacetoxysilane are used in moisture proofing masonry[83].

Organosilicon compounds like hexaethyldisilicanes, hexabutyldisilicanes and tetraheptyldiethyldisilicanes are applied along with celite for rendering window surfaces water repellent[84,85].

Aqueous silicone emulsions[86] have been used in water-proofing coating compositions for bricks, asbestos, cement, refractory materials, porous cement, etc. Several types of coating compositions based on silicone emulsions have been found useful for protecting buildings[87,88].

Water-proofing Agents

Alkoxysilicon chlorides are used for rendering hydrophilic substances water repellent[89]. For example cotton cloth immersed in 3 per cent solution of $(OC_{12}H_{25})_3SiCl$ in a mixture of ethylene and propylene chloride withstood 17 cm. hydrostatic pressure in a water repellency test, even after washing and dry cleaning.

Organosilicon esters[90], such as octadecoxydodecoxypropoxysilicon acetate, dioctadecoxypropoxysilicon acetate, dodecyldiphenylsilicon acetate and tridodecylsilicon acetate have been used for water-proofing hydrophilic solid materials. These esters are usually applied to a variety of normally hydrophilic solid materials, such as metal alloys, wood, wool, cotton or cellulosic esters or ethers to modify their surfaces and render them water repellent. For use in cotton and other cellulose based fabrics, these esters are superior to organosilicon halides. Similarly, simple organosilicon compounds like dimethyldiacetoxysilane and methyltriacetoxysilane ether[91] alone or as mixtures are used for impregnating and for water-proofing purposes.

Cohydrolysed products of methyltrimethoxysilane and ethylorthosilicate[92] and of propyltrimethoxysilane and butyltrimethoxysilane in aqueous solution are used as water repellent agents. These solutions can be applied on all types of porous materials, such as paper, wool, wood and concrete. They are neither flammable nor toxic and are suitable for use in plasters and paints.

Organosilicon amines[93] and mixtures of organosilicon nitrogen compounds have been reported to impart hydrophobic properties to different materials. For example, methylpolysilazine obtained by treating dimethyldichlorosilane and methyltrichlorosilane with liquor ammonia renders materials,

such as paper, cotton, wool, glass and ceramic articles water repellent.

Alkoxyhydrosilanes prepared by treating chlorohydrosilanes with alkoxysilanes are employed as water repelling agents for fabrics, paper and ceramic articles[94]. Siloxanes obtained from the organosilicon compounds having vinyl sulphide group[95] are used for coating siliceous materials, such as masonry, glass, asbestos or mica. Formulations based on polymethylsiloxane and methylcyclosiloxane[96], in combination with benzene, isopropyl alcohol and triethanolamine, are used for obtaining water repellent coatings on glass, wood, metal, porcelain, leather, textiles, etc. Organometallic compounds have been employed as catalysts in aqueous silicone emulsions to impart water repellency. The catalysts required for the purpose have been prepared by reacting an inorganic metal salt with an amine[97].

According to Dolgov and Voronkov[98], materials such as building lime, paint, gypsum, gypsum concrete, paper, glass, marble, limestone, etc., when treated with the vapours and/or solutions of easily hydrolysable monomeric organosilicon compounds or polysiloxanes, give non-wetting hydrophobic surfaces.

Summary

The recent developments with respect to the applications of silicone resins, particularly organosilicon compounds in cellulose, leather, glass and ceramic industries and masonry and structural works are reviewed.

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Occurrence & Activity of Protozoa in Soil

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LEEUWENHOEK was probably the first to record the occurrence of protozoa in water and soil in the seventies of the seventeenth century[1,2]. He first described a species of *Vorticella* which he had seen in standing rain water in 1675 (ref. 3). Later he gave accounts of other forms of protozoa, e.g. species of *Carchesium*, *Paramecium* and *Amoeba*[4]. During the next 150 years or so, there were apparently no reports on the subject of protozoa. Again, from about 1830 there have been occasional records of the occurrence of protozoa in soils[5].

The work of Russell and Hutchinson[6] on the effect of partial sterilization of soil on the production of plant food aroused great interest in the study of soil protozoa. These investigators reported that protozoa, such as *Colpidium cucullus* and *Amoeba nitrophila*, reduced the numbers of the beneficial bacteria in soil and thus constituted a detrimental factor in the productivity of soil. Since then, not only this effect of protozoa on bacteria but various other aspects of the protozoa in soil have also been subjects of inquiry at many centres of the world, and a large volume of literature has accumulated on these aspects. A few reviews on these aspects are available[7-14], but none of them seems to be sufficiently comprehensive or recent enough to give a fuller account of the present state of our knowledge regarding the occurrence and activity of the protozoa in soil. In this review an attempt is made to fulfil this requirement.

Occurrence of Protozoa in Soil

Examination of soils from different parts of the world[5] has shown the presence of rhizopods, flagellates and ciliates. The soils examined included those from India[15,16], England[17,18], France[19,20], East Greenland[21], Rumania[22], Scotland[23], Stockholm[24], USSR[25-28], United States[29-34], South Africa[35-40], Brazil[41], New Zealand[42,43], Jerusalem[44] and Tokyo[45]. Even samples of unproductive soils[18,41,44] and radioactive soils[38] showed the presence of protozoa.

Distribution of protozoa in different types of soil — Sherman[29,30], who examined 16 fertile soils, reported that they contained approximately 10,000 protozoa per gram, of which flagellates dominated, and ciliates and amoeba were about 1000 per gram. Waksman[31] also reported that the flagellates were the most common soil protozoa active in the soil with the moisture content too low for the development of other groups. According to Alfred[20] also, flagellates were ubiquitous, while amoeba and ciliates tended to confine to regions where organic matter was more abundant.

Koch[46] noted that in sandy loam soil, the addition of organic matter encouraged a greater protozoan development. For 10 years Fantham[39] investigated 335 South African soils in "water culture" and 114 water-logged soils. Soils containing much humus yielded more kinds of protozoa than sandy soils. The studies of Yaminoff and Zeren[25] on 21 soils from Turkestan (USSR) indicated that soils rich in organic matter contained larger numbers of species of protozoa than soils with low organic matter. The protozoa recorded were: Sarcodina — 6 genera and 7 species; Mastigophora — 12 genera and 16 species; and Infusoria — 16 genera and 21 species.

In his study of the soil protozoa of Central Asia, Brodskii[27] found that the maximum number of protozoa recorded was 1,030,000 per gram of soil, the minimum number was 10 per gram and the protozoan number diminished with the depth of the soil. He classified soils on the basis of the number of active protozoa, e.g. (i) very low activity, not more than 1000 organisms per gram; (ii) low activity, between 1000 and 20,000 per gram; (iii) moderate activity, between 20,000 and 100,000 per gram; (iv) active, between 100,000 and 500,000 per gram; and (v) very active, more than 500,000 per gram.

The earlier work of Fellers and Allison[32] indicated that poor sandy soil or forest soils contained a small number of species than soils rich in organic matter and they estimated about 5000 protozoa per gram of soil. Koffman[24] also found that although protozoa existed in normal soil, they formed an insignificant part of the micropopulation in regard to number, species and volume. Varga[47] recorded that protozoa were found in large numbers in the top humus layers of forest soils than in the lower humus-mineral layers with different species predominating. Dixon[21] observed that the richest vegetation had the highest number of species of protozoa and that an unusually large number of species of testaceous rhizopods occurred in nonpeaty soils.

Allison's[33] examination of a series of soil samples from widely divergent points in the United States showed a considerable uniformity in the distribution of the more important of the three protozoan sub-phyla, *Flagellata*, *Ciliata* and *Rhizopoda*. The range of type of genera found was quite similar to that found in English soils. Sandon's[34] results of examination of various soils near New Brunswick, New Jersey and Utah also indicated that the protozoan fauna was very similar to that occurring in English soils. Wassilewsky[26] examined 18 samples of soil from widely different parts of USSR for flagellates and there seemed to be no differences in the 11 species present in the soil samples from the extremes of locality. Guittonneau *et al.*[19] looked for protozoa in soil samples from 4 different geological formations and noted a marked similarity in the fauna, the protozoan species being common to all the 4 soils.

Masatake[45] isolated 12 ciliates, 10 flagellates, 2 rhizopods and 1 suctoria from a soil near Tokyo. Rao[15] recorded the occurrence of 25 species of

protozoa, including rhizopods, flagellates and ciliates in some soils from Mysore, India. Dixon's[28] studies on 55 soils mainly from tobacco growing areas in USSR indicated generally the presence of considerably higher numbers of rhizopods and ciliates. Of the two major protozoan groups, the rhizopods and ciliates, studied by Stout[42], the ciliates were in each soil larger than the rhizopods, and the population also appeared to be higher. Koffman[24] identified 93 forms of protozoa in a garden soil in Stockholm, and he stated that the effect of the distribution of the protozoa on soil fertility could hardly be determined without a knowledge of the kind and numbers of the forms present.

Stout[43] made a survey of the protozoa of tussock soil and pasture leaf infusions and reported that these epiphytic forms were distinct from the soil protozoa.

Rhizospheres of mangels[48], wheat[49-51], sugar beet[52], spring wheat and barley[53], cotton[54] and rye grass[23] were examined for protozoa. The results showed that the protozoan population in the rhizosphere of rye grass exceeded that in the rhizospheres of other plants. The most frequently encountered protozoa in rhizosphere of rye grass were *Cercobodo* sp., *Cercomonas* (two spp.), *Heteromita* (two spp.), *Oikomonas* sp., *Scytomonas* sp., *Tetramitus* sp., 'naked amoebae' (two spp.). There was no evidence to support Biczok's[49] statement that there were many more species of protozoa in the rhizosphere than elsewhere in the soil[23].

Similarity of protozoa in soil and water — Alfred[20] stated that the protozoan fauna in soils he examined was similar to that in fresh water. From a study of 75 cultivated, and water-logged soils in South Africa, Fantham and Paterson[35] noted that the size of rhizopods and ciliates was small in comparison to similar species found in fresh water. The later studies of Fantham[40] indicated the similarity of protozoa in soils, damp soils and fresh water. Chaudhuri[16] found that many of the species of *Rhizopoda* and *Testacea* in soil were distinctly smaller in size than the same species of aquatic forms. However, Brodskii[27] reported that soil protozoa constituted a distinct group different from the protozoa in water.

Influence of cultural practice — Martin and Lewin[18] reported that the character of the soil, water content and cultural method determined the development of the species of protozoa. A similar observation was made by Brodskii[27] who also reported that the number of species and individuals of protozoa varied greatly, depending upon moisture, temperature, season, type of soil, vegetation, cultivation, concentration of mineral salts and organic matter.

The observations of Waksman[31] indicated that (i) moisture, humus and structure of the soil were the important factors governing the activities of the protozoa; (ii) ciliates were found at a depth of 4 in., the number decreasing with the depth; and (iii) below 12 in. the soil was practically free from protozoa. Fantham[39] reported that cultivated soils tended to contain more kinds of protozoa than uncultivated soils, though exceptions occurred. Stout[43] also found that the increased soil fertility resulting from cultivation and pasture establishment was reflected partly in the increase in the number of species and partly in the "more frequent occurrence of species". However, Chaudhuri[16] concluded from his studies that *Rhizopoda* and *Testacea* were most numerous in distinctly acid soils, but otherwise no relationship could be found between soil properties and protozoan fauna or bacterial flora.

Influence of soil moisture — Cunningham[55] noted that in dry soils many encysted forms of protozoa were found than in those kept moist. Similarly, Koch[46] recorded the largest number of protozoa where the moisture was the highest; the protozoa were not active at a lower moisture content. Sherman[30] found that the number of ciliates did not increase in soil kept at its normal moisture content. Fellers and Allison[32] reported that soils rich in organic matter and of high water-holding capacity contained more number of protozoa.

Cutler and Dixon[17] showed that both in field soil and soil kept under laboratory conditions, there was protozoan activity, provided the quantity of water present was not below one-fifth of the water-holding capacity of the soil. Losina-Losinsky and Martinov[56] reported that at a moisture content of more than 20 per cent, all protozoa were extremely active. When the moisture content of the soil was comparatively low, amoebae diffused more rapidly than ciliates, but at a higher moisture content (more than 60 per cent of the water-holding capacity) the infusoria moved rapidly than the amoebae. However, Stout[42] reported that neither moisture nor food appeared to be the limiting factors and the most favourable ecological conditions obtained in the soil were with the lowest rainfall and the poorest plant cover. Nicoljuk[54] suggested that the protozoa in soil were greatly influenced by soil moisture and temperature. He found the largest numbers of individuals and species in irrigated soils.

Effect of pH — Koffman[24] found that protozoa were very sensitive to slight changes in such "physiological conditions" as pH, temperature, salt concentrations and nutrients in the culture media. But Fantham[38,39] could not find a general relationship between pH and the type and number of protozoa found in soils. Chaudhuri[16] also made a similar observation.

Effect of temperature — Cunningham[57] found that at no temperature all active forms could be killed without injury to the cysts; at 22°C. the activity of protozoa was stimulated; and at 30°C. the formation of cysts was favoured. Koch[58] reported that a temperature of 15-16°C. was most favourable for small ciliates; large ciliates would develop at all temperatures, but their maximum development was at 6-7°C. in dried blood and at 15-16°C. in hay infusion. Dixon[59] noted that 98-100 per cent cysts of *Naegleria gruberi* died in water at 70°C.; steaming the soil was usually sufficient to kill the protozoa and treatment of glasshouse soil by steam destroyed the majority of the protozoa and had a depressing effect on their numbers for a long period. Singh[60] found that even heat (even maintaining a temperature of 58°C. for 30 sec. followed by quick cooling) killed many encysted soil protozoa as well as the active forms. Bodenheimer and Reich[44] gave evidence that cysts

of soil protozoa might also show under different environmental conditions "an entirely different tolerance" for heat and the degree of dehydration of the cysts was especially important in this respect.

Effect of chemicals — Cutler[61] exposed soil overnight to a 2 per cent solution of hydrochloric acid and reported that, at the end of the exposure, all active protozoa were dead, but no cysts were damaged. But Bodenheimer and Reich[44] showed that the cysts of at least some of the soil protozoa became decidedly damaged by treatment with hydrochloric acid. However, Singh[60] later found that treatment with 2 per cent hydrochloric acid destroyed the active forms of soil protozoa without destroying any appreciable numbers of encysted forms.

Dixon's[59] experiments to discover 'the death point' of protozoa by phenol and carbon bisulphide showed that phenol had greater lethal effect, 0·1 per cent concentration being sufficient to kill active *Hartmanella hyalina* and *Cercomonas crassicauda*. Carbon bisulphide at 1 per cent concentration had no ill-effects on the cysts of *Hartmanella hyalina*.

Baumgartel and Butenschon[62] noted that heavy applications of potash to soil promoted more favourable conditions for the development of protozoa. Singh[63] studied the effect of artificial fertilizers and dung on the numbers of amoebae in Rothamsted soils. He found that the total numbers (active *plus* cystic) and the numbers of active amoebae in plots treated with complete minerals plus ammonium sulphate and with farmyard manure were much higher than in the untreated plots. The complete minerals plot of Barnfield had a just significantly lower total count of amoebae than the farmyard manured plot, although no significant difference existed between the counts of active amoebae. The difference in the numbers of both the total and active amoebae between the complete minerals and farmyard manure treated plots on broadbalk was not significant. No correlation was found between the percentage of organic carbon in the soils and the number of amoebae.

In the course of his studies on the toxic effects of certain bacterial metabolic products on soil protozoa, Singh[64] found that a chloroform extract of *Bacillus pyocyaneum* was "very toxic in high concentrations to soil amoebae, flagellates and ciliates, which were killed in a few minutes". Chemically pure pyocyanine and α-hydroxy phenazine were less toxic to soil protozoa than the crude chloroform extract. Later Singh and Crump[65] showed that formalin-treated soil had significantly lower numbers of amoebae as compared to the untreated soil over a period of one year, although the bacterial numbers were often higher than those in the latter. They suggested that "the unsuitable quality of bacterial food supply" might be responsible for keeping the numbers of amoebae in check in the formalin-treated soil. "Double-formalin treatment" seemed to suppress further the numbers of amoebae.

Are the Protozoa Active in Soil?

Goodey[66] stated that ciliated protozoa could not function as the factor limiting bacterial activity in the soil, as ciliated protozoa existed in the soil in an encysted condition. Fellers and Allison[32] inferred that in normal New Jersey soil the protozoa existed only in a non-trophic state. Alfred[20] reported that no active forms occurred in dry soil. Koffman[24] studied the development of cysts of aquatic protozoa that did not belong to the active inhabitants of the soil and inferred that protozoa occurred only in an encysted state.

However, Martin[67] was able to follow the life cycle of a flagellate monad in a sick soil. Later, he[68] used "the picric acid fixation method" and found that the protozoa were leading a trophic life in the soil studied at the date of fixation. Martin and Lewin[69] collected further evidence to prove the existence of a trophic protozoan fauna in certain soils. They[18] also showed that the soil protozoa existed in three states: (i) the active fauna, (ii) the resting fauna as cysts, and (iii) "the cultural fauna". They added that seasonal variations might result in a transfer of certain forms from one state to the other. Cunningham[70] reported that at least some of the soil protozoa led an active life and were capable of multiplying to quite a considerable extent under favourable conditions.

Cutler[71] used the direct counting method and showed that protozoa in the soil were in a trophic state. With the aid of phenolsulphonaphthalein stain, Itano and Ray[72] found that direct examination of the trophic soil protozoan forms was possible. Koffman[24] also reported that in normal soils small flagellates and amoebae were constantly found both in vegetative and cystic conditions. Kino[73] concluded from a study of the farm lands of Japan, which were heavily irrigated for rice culture, that the activities of ciliates were greatly increased.

In considering the question, "Are there any soil protozoa?", Sandon[74] drew attention to the experimental work of Cutler at Rothamsted and explained the reasons for the failure to observe protozoa in soil by microscopical examination and also indicated the methods by which the occurrence of active protozoa in soil could be demonstrated. Later, Sandon[5] stated that the "earlier objections based on the belief that the protozoa were present in the soil merely as stragglers brought in accidentally from other more natural habitats, existing for the greater part of the time only as inert cysts and incapable of taking any active part in the life of the soil community, have now been entirely removed by the demonstration that, at any rate in the soils of temperate climates, they are present at all times of the year, leading an active life, often attaining very high numbers, and undoubtedly constituting an important component of the soil population". The studies of Brodskii[27] also showed that the protozoa were physiologically active in the soil except under conditions of extreme dryness.

Counting and Culturing of the Soil Protozoa

Counting — Koch[58] modified "the loop method" (using a platinum wire bent into a permanent loop) for counting the protozoa in soil, which was originally employed by Müller[75] for counting bacteria. The quantity of solution that could be transferred

from the sample by means of this modified loop was then determined by carefully weighing films of the culture solution on a sensitive analytical balance. The average of several weights was taken and the quantity of liquid transferred by the loop was calculated into cubic centimetres. A film of the culture solution containing the living protozoa was then transferred to the ruled area on the clean glass slide. In this manner the living protozoa were counted under the low power of the microscope, and from the number of organisms transferred in the loop the numbers per cubic centimetre were calculated.

Itano and Ray[72] made direct microscopic counts of the protozoa in the films of the soil suspension thickened with gelatin, using phenolsulphonaphthalein referred to earlier. Cutler[71] employed the method of Kopeloff *et al.*[76] for making direct counts of the soil protozoa in the liquid medium. This method consisted in directly estimating the numbers of protozoa in a suspension which did not involve plating on culture media and subsequent incubation. According to Cutler[71], this method was satisfactory when compared with the dilution method used at Rothamsted.

Culturing — Goodey[66] cultivated protozoa in soil extract and dilute hay infusion. Martin and Lewin[69] used horse manure and agar for the cultivation of the protozoa. Rahn[77] employed peptone and sugar solutions for the organisms to develop in a culture solution of 1-100 dilution for 7-14 days.

Killer[78] used the dilution method to determine the appropriate numbers of soil protozoa that developed in " Giltay's mannite and peptone solutions ". Cauda and Sangiorgi[79] employed " Giltay's, Omelianski's, Hiltner's peptone and mannite solutions " and determined the numbers of organisms by dilution and direct count. Cunningham and Lohnis[80] tried several culture solutions for the growth of soil protozoa and finally Cunningham[70] found that soil extract and blood-meal extract constituted a better medium.

Koch[58] conducted numerous experiments under different soil conditions and showed that the maximum development of ciliates and flagellates depended on the culture solution, the amount of soil used and other conditions. Soil extract seemed a little more favourable than blood extract for the development of all forms of protozoa.

Sandon[5] used nutrient agar, dilute hay infusion and sterile tap water and examined the cultures weekly for three weeks.

Dixon[81] used peptone agar, soil extract agar, hay infusion and soil extract for counting the protozoa in 55 Russian tobacco soils. A more varied protozoan population developed in soil extract and on soil extract agar, both of which gave much higher protozoan numbers than peptone agar and also showed an increase in the species and individuals of amoebae. However, the peptone agar medium favoured the development of the common types of soil protozoa. The investigation also showed that the use of soil extract agar as a medium for the growth of protozoa gave a truer picture of the soil protozoan fauna than the use of peptone agar. Dixon[28] later reported that soil extract agar and liquid soil extract as media gave the fullest record of protozoa, particularly the rhizopoda and ciliata. Hay infusion was useful for the development of the ciliates and it was a better medium than peptone agar. Ciliates were rarely found on the peptone agar.

Experiments in this laboratory showed that autoclaved sewage may be used as a medium for the cultivation of the soil protozoa, more especially the ciliates. The medium may preferably be artificially aerated for varying periods, from 48 to 120 hr, and the protozoa be counted with the aid of a microscope.

Influence of Protozoa on Soil Conditions

Protozoa as a factor in the 'sickness' of soil — Russell and Golding[82] concluded from their investigations on 'sickness in soil' that there were two distinct sets of causes in sewage-sick soils: physical causes that led to retarded percolation, and a factor detrimental to bacteria. The factor detrimental to bacteria was in every respect similar to that shown by Russell and Hutchinson[6] to exist in ordinary soils. Its effects were, however, much more pronounced in sewage-sick soil than in ordinary soil. Sewage sickness was thus regarded, in part, as an abnormal development of the harmful factor always present in ordinary soils. Examination of the soil for possible destructive organisms showed the presence of *amoebae*, and a *vorticella* (*V. putrina*) and other protozoa which, so far as they are active in soil, would destroy bacteria; monads were also found — *Euglena* and others[83].

Martin and Lewin[69] supported the view of Russell and Hutchinson[6] that the protozoa, which were present in sick soils, did exercise an important influence on plant growth in these soils. The results of the investigations of Laszlo Telegdy-Kovats[84] also justified a direct application of Russell and Hutchinson's theory. Hino[85] further confirmed that abundant existence of the protozoa and their strong activity induced soil sickness.

On the contrary, the results obtained by Goodey[86] warranted the conclusion that ciliates, amoebae, and flagellates could not be included in the biological factor described by Russell and Hutchinson[6]. He gave further evidence that the presence of 10,000 amoebae per gram of soil was not sufficient to reduce the bacterial content of a soil to the level of a similar soil containing no protozoa even though the soil was kept under conditions of moisture, etc., favourable to the trophic existence of amoebae and flagellates. Russell[87] pointed out in this connection that until more was known of the kinds of protozoa occurring in the trophic state in the soil and of their life-history in the soil, it would not be possible to lay much stress on " the negative results of re-infections ".

Sherman[30] recorded that a comparison of treated and untreated soils under various conditions failed entirely to give any evidence in support of the theory that there existed in soil a harmful biological factor which was destroyed by the action of volatile

antiseptics. Accodring to Piettre and De Souza[41], the progressive sterility of the soils studied was due not to protozoa or bacteria, but to the toxic products present in the soils.

Kino[73] showed that the protozoa studied in farm lands of Japan, which were heavily irrigated for rice culture, did not greatly affect the activity of soil organisms in general. Koffman[24] reported that the improvement in soil fertility following sterilization of the soil was due, not to the killing of the protozoa, but to other factors. True soil protozoa, according to him, would not seem to exercise any appreciable effect on the number of bacteria or on other soil microorganisms in normal soil. Moreover, in abnormal conditions (water-logged soils or sewage-irrigated soils) they might check the development of bacteria and were " important for such soils' metabolisms ".

The observations of Pillai *et al.*[88] on sewage-sickness of soil showed that, although there might be a number of individual factors leading to diminished crop yields and other features associated with sewage-sickness, the most important factor which predetermined such effects was the extent of air supply to plant roots. If liberal air supply to plants could be ensured through one of the various treatments studied, all the other influencing factors were practically eliminated, and there could be healthy and even luxuriant growth of plants. In the reclamation of sewage-sick soils, therefore, the foremost consideration should be given to conditions favouring improved soil aeration.

Effect of protozoa on soil processes in general — Müller[89] reported studies concerning some soil protozoa which he thought played a part in the destruction of ' organic tissue ' and were considered important agents in the formation of humus. Wolff[90] attributed various functions to the protozoa, viz. (1) carrying disease germs; (2) taking up and killing algae, fungi, and bacteria; (3) absorption of useful material from the soil water, thus preventing it from sinking to the deeper layers of soil; and (4) power of living at all seasons of the year, so long as the ground was sufficiently moist and was not frozen. Varga[47] inferred that Rhizopoda and Mastigophora played the most important role in the decomposition of organic matter on account of their great abundance in humus layers.

Skinner[91] recorded that when *Hartmanella hyalina* was inoculated to a partially sterilized soil, there was a slight depression in the evolution of carbon dioxide. Cutler and Crump[92] stated that, provided amoebae were present, carbon dioxide and bacterial numbers could be correlated and that the amoebae caused a decrease in carbon dioxide production in sands treated with peptone, but an increase in sands treated with mineral salt solution with glucose or soil extract.

After several years of investigation of the soils in Central Asia, Brodskii and Beliaeva[93] concluded that the activity of protozoa was a good indicator of the degree of activity of soil processes.

Tracey[94] showed that *Hartmanella glebae*, *Hartmanella* sp., *Schizopyrenus erythaenusa* were the only soil protozoa that possessed cellulase and chitinase activities and that ruminant ciliates were known to decompose cellulose. He suggested that many other soil protozoa might be active enzymatically.

Influence of protozoa on the bacterial numbers in soil — Cunningham[57,70] concluded from his results that soil protozoa in culture solutions exercised a very decided limiting effect on the numbers of bacteria and that this reduction was well outside the limits of experimental error. Waksman[31] also showed that the presence of protozoa acted detrimentally upon bacterial numbers.

Cutler[95] reported that in a normal field soil the bacteria and active " amoebas " had an inverse relationship. Cutler and Crump[92] showed that the rate of growth of amoebae, as measured in numbers or mass of protoplasm, was proportional to the numbers of bacteria. According to them[96], it was established that the presence of protozoa prevented the bacteria from attaining to as high a level as they would in a soil devoid of protozoa.

Skinner[91] showed that *Hartmanella hyalina*, when inoculated to a partially sterilized soil, caused a reduction in the number of bacteria. Losina-Losinsky and Martinov[56] found that bacteria, in their progressive movement, always preceded the protozoa; the bacteria (*Bacillus radicicola*) served as a source of food for the protozoa. Meiklejohn[97] recorded that in sand cultures the presence of amoebae lowered the bacterial numbers. Baumgartel[98] reported that soil protozoa were found actively feeding on the bacteria in the surface film of the culture.

At the same time, there have been reports to the effect that there was no reduction of bacteria in the presence of protozoa. Thus, Sherman[30] reported that protozoa did not have a limiting action on the bacterial flora in the soils studied under varying moisture content and temperature. Koch[46] found no correlation between the numbers of active protozoa and the numbers of active bacteria.

Thais and Gurfein[99] noted that when mannitol was used, the bacterium, *Azotobacter*, developed much better in the presence of amoebae. Similarly, Hervey and Greaves[100] reported that *Azotobacter* were much more numerous in the presence of protozoa, both in liquid and soil cultures.

Cutler and Crump[92] showed that the filtrate from an old bacterial culture " having low feeding value " retarded the development of *Hartmanella hyalina* when added to a culture of " high feeding value ". Singh[64] found that the pigment extracted from *Serratia marcescens* and *Chromobacterium violaceum* and from a red pigmented bacterium when mixed with edible bacterial suspensions on agar apparently prevented amoebae from ingesting the bacteria, whereas non-pigmented strains of *S. marcescens* were completely destroyed by the amoebae.

Drozanski and Drozanska[101] reported that Gram negative microorganisms, which were killed at 100°C., were unsuitable as food for soil amoebae. However, extracts from disrupted *Aerobacter* or yeast cells stimulated the ingestion of Gram negative microorganisms killed at 100°C. and made them suitable as food for amoebae. Drozanski[102] later showed that the extract of disrupted bacteria or some amino acids inhibited encystment of the soil amoebae.

Influence of Protozoa on the Nitrogen Changes in Soil

Nitrogen fixation — Hills[103] stated that the protozoa did not have a detrimental effect on the process of "free nitrogen fixation in soil". Nasir[104] reported that the presence of protozoa played an important part in the fixation of atmospheric nitrogen by *Azotobacter*. Cutler and Bal[105] reported an increased nitrogen fixation by *Azotobacter* in the presence of *Colpidium colpoda* and *Hartmanella hyalina*. Hirai and Hino[106] showed that protozoa stimulated nitrogen fixation by *Azotobacter*. Thais and Gurfein[97] noted that when amoebae and *Azotobacter* were grown together, amoebae were found to feed on bacteria and lead to a stimulation in the multiplication of *Azotobacter*. Laszlo Telegdy-Kovats[84] showed that the presence of *Colpidium* and *Paramecium* had a stimulatory effect on *Azotobacter* on the fixation of atmospheric nitrogen.

Kino[73] reported that the protozoa studied played a role in nitrogen fixation and in decrease in soil acidity. Hervey and Greaves[100] found that the protozoa generally stimulated nitrogen fixation; the stimulation was greatest in the presence of ciliates in the liquid medium and the increased nitrogen fixation as well as increased *Azotobacter* cells in the presence of protozoa were probably brought about by a thermostable complex organic colloid elaborated by the protozoa.

Ammonification — Hutchinson[107] found that rapid nitrification took place when green manure was placed in water and allowed to ferment and that this was accompanied by the development of large numbers of ciliates, flagellates and amoebae whose presence did not appear to be prejudicial to the activity of the ammonifying bacteria. He conceded, however, that this might be especially due to active multiplication of bacteria. The studies of Cunningham on the influence of protozoa on ammonification in "solution tests", however, did not justify any definite conclusion. Hills[103] heated a soil at 90°C. for 1 hr and then inoculated with 1 per cent of the original untreated soil, and he found that the supposed harmful factor, namely the protozoa, had no detrimental effect on the formation of ammonia and on its subsequent oxidation to nitrate. Waksman[31] also found that protozoa did not have any appreciable influence on ammonification by bacteria.

On the other hand, Skinner[91] reported that *Hartmanella hyalina* caused ammonia accumulation when this protozoan was inoculated to a partially sterilized soil. Meiklejohn[97] reported that in sand cultures the presence of amoebae lowered the bacterial numbers, but it appeared to increase the rate of ammonia formation. It was suggested that the amoebae reduced the bacterial numbers from too high a value to a value nearer the optimum for ammonia formation and thus increased the rate of ammonia formation.

Antagonistic action of protozoa against plant pathogens — Kino[73] suggested that protozoa played a role in the destruction of plant pathogens. Hino[85] considered that the protozoa were "very strong in antagonistic action to plant pathogens".

Weber *et al.*[108] reported an unidentified predacious amoeboid organism which destroyed the larvae of nematodes attacking the potato roots.

Discussion

Although there have been records of protozoa in waters and soils since the early years of the invention of microscope, it was not until after the report of Russell and Hutchinson[6] in 1909 that serious interest in the soil protozoa has been taken. Russell and Hutchinson called attention to the protozoa as a factor prejudicial to the productivity of soil, and they were led to do so mainly on two grounds: firstly, the occurrence of a variety of protozoa in heavily manured soils and also in sewage-sick soil, which were found to devour bacteria; and secondly, the increased formation of ammonia closely following the destruction of the protozoa and the great increase in bacterial numbers.

In the sixties of the last century great advances were being made in bacteriology, and Pasteur expressed the opinion that nitrification was a bacterial process[109]. The next few decades saw the isolation of ammonifying, nitrifying and nitrogen fixing bacteria from soil and the study of their usefulness. At the same time several protozoa parasitic on man and animals were discovered and seriously studied. Whether or not these parallel lines of work on bacteria and protozoa had any influence on the development of the view that the protozoa in soil are harmful to the useful bacteria, the experiments of Russell and Hutchinson evoked a great deal of work on soil protozoa, which was sustained for many years.

Several investigators have given evidence that practically all soils of the world contain protozoa either in an active state or as cysts. Fertile or productive soils contain the maximum number of active protozoa, as their activity is apparently dependent on optimum moisture, temperature, *p*H and on other factors like the absence of toxic substances in soil.

The views regarding the protozoan control of bacteria in soil are rather conflicting. Russell and Russell[109] stated that: "There must presumably be a relation between the numbers of protozoa and of bacteria present in the soil since certain species of bacteria are the principal source of food for the protozoa, but this subject has received little attention recently, and the results of the older work are unreliable as the techniques used for counting were inadequate. Hence no reliable estimates can yet be made of the numbers of bacteria that are consumed daily by the protozoal population". There is also the more important question whether such a control of the bacteria is of any significance in soil economy.

More clear evidence on soil protozoa would have resulted if there had been better methods of isolation and cultivation of protozoa, which live notably in the company of bacteria. Preparation of pure cultures of protozoa has seldom been achieved. With the methods available for culturing protozoa, a few workers have shown that certain forms of protozoa have a beneficial influence on the nitrogen

fixing bacteria. A few others have shown that some protozoa preferentially consume certain specific bacteria.

Thus, while there is considerable evidence on the occurrence of protozoa in soils under favourable conditions, there is no definite information on their activity. According to Sandon[5], "As to the role played by them in soil economy, however, it must be confessed that the work of these seventeen years has yielded disappointingly little really convincing information". Stevenson[110] stated that "the protozoa remain a virtually unknown quantity in soil". According to Bortels[111], "of the animal unicellulars, the protozoa, we do not know much more than that they feed not only on dead organic matter, but also on living bacteria, thus constituting perhaps an important regulating factor like the tiny predatory bacteria".

It may be useful to consider whether the available knowledge of the principles of sewage purification is applicable to the study of soil processes. It was one of the earliest studies carried out by Scholesing and Muntz[112] in 1877-78 on the purification of sewage by land filters that gave rise to the concept of microbial activity in nitrate formation in soil. Russell[113] stated that many of the nitrogen changes in soil closely resembled those occurring during sewage purification, as worked out by Adeney[114] and Fowler[115], one of the main differences being that they proceeded more quickly in sewage than in soil.

In discussing the possibility of converting ammonium salts into nitrates by bacteriological processes, Makrinov[116] compared nitrification in soil and in the activated sludge process of sewage disposal, and stated that nitrification took place much more rapidly in the latter system than in the former. He stated that: "By the use of an activating substance, similar to the film in the activated sludge, and aeration, it is possible to utilise the process of nitrification for the oxidation of $(NH_4)_2SO_4$." According to Fowler[117,118], "the changes which go on in an activated sludge tank are essentially the same as those taking part in an arable soil. Activated sludge contains forms of life almost identical with those found in fertile soil. Seasonal variations among these are similar to those which have been observed in the course of prolonged studies of soil phenomena at Rothamsted. The effect of selective antiseptics in inhibiting the growth of protozoa with the consequent increase in the bacterial population is much the same in activated sludge as in soil. Both soil and activated sludge must be considered as living systems if they are to be properly 'managed'."

Moreover, evidence is accumulating in the Department of Biochemistry at the Indian Institute of Science, Bangalore, that simple and colonial vorticellid ciliate protozoa, such as the species of *Vorticella, Carchesium, Zoothamnium, Epistylis* and *Opercularia* play a vital role in the rapid flocculation or clarification of sewage, nitrification, nitrogen conservation and other changes as observed in the activated sludge process[119-124]. These protozoa develop in "oxidizing filters"[125], in the effluents from filters[126], in land-filtered sewage effluents[127,128], and during vigorous flow of sewage on land[129,130]. The protozoa in sewage under aerobic conditions have been traced to the soil[127,131]. Species of *Vorticella* and *Epistylis* are known to occur in arable soils, rich green house soils, and in pasture soils[5,32,66] and species of *Carchesium* are also known to occur in soils[15]. Ordinarily these protozoa exist as cysts in soil, as their development is limited by the amount of water, nutrients and by other conditions. Certain forms of protozoa, such as small ciliates, may be actively present in soil.

When cultures of actively growing protozoa, such as *Colpoda* sp., were introduced into the soil treated with sterilized sewage matter and maintained at about 50 per cent moisture, they were found to collect on them the soil bacteria and other materials in the soil, including fine silt and clay. As a result of such aggregating or flocculating activity of the protozoa, it was observed that the pore space of the soil system increased considerably. Thus, in one series of experiments in which a culture of *Colpoda* sp. was used, there was an increase of about 8 per cent in the pore space of the soil system (increase over the control series of soil samples in which the protozoan culture was not introduced)[11].

Hardin[132] recorded a clear-cut instance of flocculating activity of the ubiquitous fresh water and soil flagellate, *Oikomonas termo* Kent. This protozoan, when grown in two-membered culture with various bacteria in liquid medium, caused a very marked flocculation of *Erwinea carotovora, Erw. phytophthora, Proteus vulgaris, Phytomonas tumefaciens* and one strain of *Escherichia coli*. Microscopically, each of the floccules (about 3 mm. diam.) consisted of a large mass of bacteria with a few flagellates attached at the periphery. He concluded that "since both the bacterial and protozoan cultures used for the inoculations were pure cultures, and since the bacteria when grown alone in this medium flocculated very slightly, and then only in old cultures, there can be little doubt of the causal significance of the protozoan". Another report relevant here is that of Watson[133] who followed anabiosis in a soil ciliate, *Balantiophorus minutus* Schew., which is "peculiarly well fitted for life in the surface soil, where the amount of free water is subject to frequent and drastic alteration, and is at all times limited save in water-logged soils". In agar plate cultures of this ciliate, it was observed that it could remain active in very restricted films of water, wriggling between bacterial masses on the surface of the agar in an almost amoeboid fashion and that it caused flocculation of the bacteria, similar to the flocculation caused by *Oikomonas termo*[132] and by *Epistylis* and *Vorticella*[121].

The foregoing observations would suggest a new approach to the investigation of the activity of soil protozoa, if there was precise information on the protozoa characteristic of all healthy and productive soils. A primary effect of the protozoan activity in the soil environment may possibly be on its physical condition which promotes pore space, but evidence on this and related aspects has to be collected, if there is a protozoan fauna for arable soils of the world.

Summary

The available information on the occurrence and distribution of protozoa in soils, the factors influencing their development, the methods of counting and culturing them and on the nature and extent of their activity, particularly their effect on bacterial numbers and nitrogen fixation, is reviewed. The evidence on the protozoa, both in relation to a possible distinctive group in productive soils and to their normal activity in the soils, is inadequate.

There is some similarity between the protozoa in natural waters, including polluted waters like sewage, and soils, and there is a close resemblance of the changes in aerated sewage and in arable soil. It is, therefore, suggested that the methods and techniques employed to study the occurrence and development as well as the flocculating and oxidizing activity of the protozoa in sewage purification systems may be usefully applied in the investigation of the soil protozoa.

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Microbial Degradation of Pectic Substances

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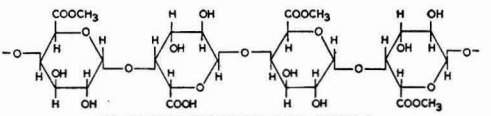
EVEN though the discovery of pectin by Vanquelin[1] could be traced back to 1790, the concept of its degradation due to the agency of microorganisms was realized by Mitscherlich[2] only six decades later. Since then a large body of information has accumulated on a wide variety of microorganisms capable of attacking pectic substances. A critical appraisal of the reports dealing with these macromolecules, the utility, chemistry, occurrence and mode of action of the pectinolytic enzymes thereon, laying, at the same time, emphasis on the developments that have taken place during the past decade and a half forms the subject matter of this review.

Utility of Pectic Substances

Though pectic substances find use in food and food products, pharmaceuticals and cosmetics and in bacteriological media because of their congealing properties, their removal from food products and industrial raw materials by the action of pectinolytic enzymes of microorganisms is of great economic importance. Commercially the pectic enzymes are used widely for the clarification of fruit juices, wine[3] and in the preparation of certain products like instant coffee. Pectinolytic flora play an important part in the retting of textile and other plant fibres. These organisms also cause plant diseases, and are suspected to have a role in the fermentation of such products as tobacco, cocoa and coffee beans[4-9].

Chemistry of Pectic Substances

The pectic substances are complex colloidal carbohydrate derivatives of plant origin containing a large portion of anhydrogalacturonic acid units believed to occur in a chain-like combination. The uncertainty of shape and size of these complex polymers is of such a magnitude as to create some confusion in an otherwise uncomplicated branch of carbohydrate chemistry. The evolution of ideas concerning the composition and structure of these substances may be seen in the excellent treatise by Kertesz[3] or in other reviews[10-18]. However, the terminology adopted by the American Chemical Society[19] has gained universal acceptance in classifying the pectic substances and is the one used in this review. Accordingly, 'protopectin' represents the water insoluble parent pectic substance which occurs in plants and which, on restricted hydrolysis, yields pectinic acids. While the term 'pectinic acids' is used for colloidal polygalacturonic acids containing more than a negligible proportion of methyl ester groups, the general term 'pectin' designates those water soluble pectinic acids which have varying methyl ester content and degree of neutralization. The term 'pectic acid', on the other hand, is applied to pectic substances



(I): PECTIN (WITHOUT END UNITS)

composed mostly of colloidal polygalacturonic acids essentially free of methyl ester groups.

The concept of a linear structure for the basic unit in pectin was suggested by Morell *et al.*[20], but the spatial relationship represented in the hexagonal formula of Haworth[3] (I) is better suited and more widely used. The molecules of pectic acids have been known to contain D-galacturonic acid units linked together through α-(1-4) glycosidic linkages and, irrespective of the sources from which they are derived, such molecules are essentially similar[21,22]. Although their basic structure has been recognized as that representing polygalacturonic acid, no agreement has been reached on the exact chemical nature of the natural pectins. Whereas some workers consider pectic substances as composed of carbohydrate moieties or certain groups attached to the chains of anhydrogalacturonic acid units[23-26], others, including Kertesz[3], are inclined to believe that the non-uronides do not belong to these and may, in fact, be impurities that merely accompany them[27-31].

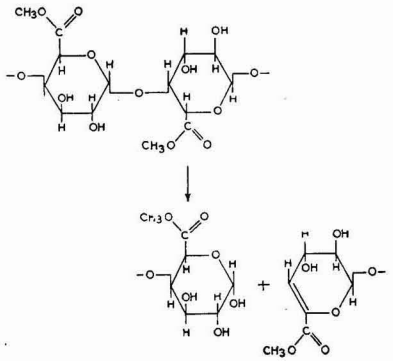
Pectinolytic Enzymes

The information available on the enzymes catalysing degradation of pectic substances is extensive and has been the subject of several reviews[32-39]. Five pectinolytic enzymes have so far been recognized: protopectinase, pectin methyl esterase, polygalacturonase, pectic acid depolymerase and pectin *trans*-eliminase. The first one is rather ill defined and is believed to act on the insoluble parent pectic substance protopectin, resulting in the formation of soluble pectin and consequent maceration of the plant tissues. As the nature of protopectin itself is not clear, the demonstration of its dissolution by the enzyme can only be ascertained by following its action on plant tissues without seeking to explain the chemical reactions involved. The present tendency is to believe that both protopectinase and polygalacturonase are one and the same enzyme, a view consistent with the assumption that protopectin is either a modification of pectinic acid or is composed of very large molecules of pectinic acid. It is also not uncommon that many microorganisms producing one or the other of the polygalacturonase can bring about the solubilization of protopectin and the maceration of tissues.

Pectin methyl esterase is a hydrolase which catalyses a cleavage of methyl ester groups of pectins and pectinic acids and its activity results in the

formation of pectic acids and methanol. Polygalacturonase is another hydrolase, but the term is used in a wide sense and includes all glycosidases which bring about the hydrolysis of glycosidic bonds in pectic substances. Demain and Phaff[40] proposed a general scheme for their classification, but admitted it to be only a tentative one; from all accounts it would seem, however, that the breakdown of pectic substances is brought about by a β-elimination mechanism[41,42] discovered subsequently. Nevertheless, such of those enzymes which cause a hydrolytic cleavage of glycosidic bonds in pectic substances could be classed among polygalacturonases. Pectic acid depolymerase differs from polygalacturonase in having a sharp *p*H optimum at 4·5; besides, it gets activated by NaCl.

Newly discovered among the pectinolytic enzymes is the pectin *trans*-eliminase and a comprehensive review thereon has appeared only recently[43]. This enzyme brings about the formation of 4-5 unsaturated compound from pectin by way of *trans*-elimination reaction which involves the removal of hydrogen atom at C-5 and glycosidic residue at C-4 to the ester carbonyl group (Scheme 1). This enzyme was discovered in the course of investigations on the alkaline degradation of pectin[44,45] and its presence was primarily demonstrated in a commercial pectinase preparation ' Pectasin R-10 '[42] and subsequently in a wide variety of microorganisms[46-56]. An explanation of the mechanism of this degradation was offered on the model of β-dealkoxylation involved in the breakdown of polysaccharides[44].



Scheme 1 — Action of pectin *trans*-eliminase

Degradation of Pectic Substances by Different Microorganisms

Pectic enzymes have been demonstrated in a wide variety of sources as fruits[3,57], germinating barley[3], hepatic and pancreatic secretions of water, garden snails[3], etc. Humans and other vertebrates lack these enzymes. Their widespread occurrence in microorganisms is dealt with under the following heads.

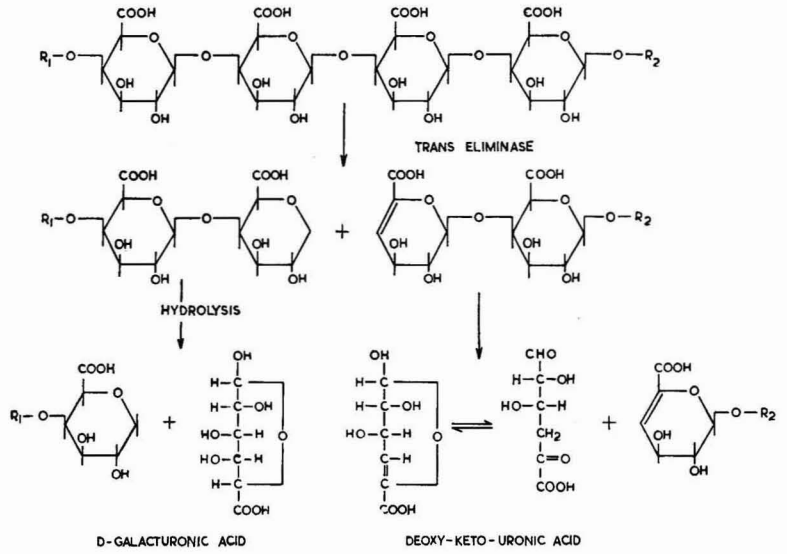
Anaerobic Bacteria

Microbiological examination of the ret liquors of *Hibiscus cannabinus* and *Malachra capitata* L. resulted in the isolation of *Clostridium butyricum* var. *pectinovorum* and certain pseudomonads[58-60], both of which were capable of attacking pure pectins. Wieringa[61] isolated *Cl. pectinovorum* from the rets of flax and noted that the optimal production of pectinase occurred at neutral *p*H. The taxonomic aspects of this group of organisms were discussed by Raynaud[62] and more recently by Lanigan[63]. Subsequently, Ng and Vaughn[64] observed that pectinolytic anaerobes constitute a heterogeneous group, though they belonged to the same genus *Clostridium* and resembled closely *Cl. butyricum, Cl. fallax, Cl. multifermentans, Cl. indolis* and *Cl. rubrum* n. sp. All were, however, pectinolytic. The discovery of the new enzyme pectin *trans*-eliminase was soon followed by that of polygalacturonic acid *trans*-eliminase in a strain of *Cl. multifermentans*[51,52], the latter having the ability to attack the terminal groups to produce a preponderance of unsaturated digalacturonic acid.

Aerobic Bacteria

A careful scrutiny of 17 Scottish soils led to the finding that the dominant soft rot organisms of the soils comprised pseudomonads[65] rather than coliforms, as was believed to be the case earlier[66]. However, the techniques used in both the investigations were identical. Similarly, screening of 400 strains of *Pseudomonas* isolated from a variety of sources as soils, water, the gut of earthworms and plants (both diseased and healthy) suggested the possible role pseudomonads have in the degradation of pectic substances[67]. Isolation of certain fluorescent *Pseudomonas* from flax rets prompted Wieringa[68] to believe these isolates to be of greater importance than *Cladosporium herbarum, Cryptococcus albidus, Rhodotorula glutinis* and *R. macerans* in this retting process. However, it was left to Betrabet and Bhat[59,60] to furnish clear evidence in favour of the pectinolytic activity of *Pseudomonas* and their possible role in the degradation of plant straws. Supporting evidence in favour of this view came forth later[69]. The main difficulty which arose in bringing evidence in favour of *Pseudomonas* and other bacterial species as pectinolytic was the loss of activity which occurred in cultures stored in the laboratory. In fact, the cultures clearly proved to be pectinolytic by Betrabet and Bhat[59,60] were found by them to be not so after a few months' storage, notwithstanding the fact that the maintenance medium contained pectin. Subsequent work carried out in the laboratory has, however, shown the way to preserving the pectinolytic activities of the bacterial cultures by resorting to the use of polygalacturonate, rather than to pectin, in the storage media[70].

Preiss and Ashwell[71,72] worked out the metabolic pattern of a pseudomonad adapted to polygalacturonic acid and observed the accumulation of two monosaccharide end products, D-galacturonic acid and 4-deoxy-4-threo-5-hexoseulose uronic acid (Scheme 2). Recent work on bacteria which clearly belong to Pseudomonadaceae, viz. *Aeromonas liquefaciens*, has indeed revealed the presence of pectin *trans*-eliminase in them[55,70,73].



Scheme 2 — Polygalacturonic acid metabolism in *Pseudomonas* sp.

Sabet and Dowson[74] were perhaps the first to show that the genus *Xanthomonas* contains pectinolytic species. These workers attributed to *X. campestris, X. citri, X. malvacearum* and *X. begoniae* pectinolytic property by employing a technique demonstrative of the pectate gel liquefaction. An extensive survey of the pectinolytic enzymes of this genus brought to the fore the ability of 38 species (of the 145 cultures tested among which as many as 75 cultures were pectinolytic) to elaborate the enzymes pectin methyl esterase, polygalacturonase and protopectinase[75]. Subsequent investigations resulted in the successful isolation of several pectinolytic *Xanthomonas* from sewage[76]. More interesting, however, was the demonstration that pectinolytic species of the genus possess not only a strong polygalacturonase but also a hitherto unrecognized mode of attack on pectic substances[77]. The *trans*-eliminative mechanism was shown to occur in this genus by Starr and Nasuno[78].

Attention to the genus *Flavobacterium* was drawn by Dorey[79] who found pectinolytic species of this genus to possess polygalacturonase but not pectin methyl esterase. The more recent isolation of *Flavobacterium* sp. by the exploitation of enrichment culture technique and the detection of pectinolytic activity in the isolates are notable features[80]. The presence of the enzyme *trans*-eliminase in some of them was also witnessed in this laboratory[55]. The ability of coli-aerogenes group to degrade pectic substances is not altogether convincing, notwithstanding the fact that several reports on the occurrence in nature of pectinolytic species are available in literature. In fact, Smith[81] pointed out the production of polygalacturonase in bacteria belonging to coliform group. Similar observation on the occurrence of pectinolytic bacteria belonging to the genera *Escherichia* and *Aerobacter* was made by others[82,83]. Evidence in support of this view was also obtained by three others working in this laboratory[76,80,84]. That the production and secretion of polygalacturonase by *Erwinia carotovora* was greatly increased by the addition of pectic substances into growth medium was observed by Kraght and Starr[85]. The inducible nature of the pectinolytic enzymes of *Erwinia* sp. was also observed by Ozawa and Okamoto[86]. Starr and Moran[49,50] subsequently demonstrated that *E. carotovora* contained a potent *trans*-eliminase system distinct from that met with in certain other species of the genus which show cleavage of molecules of unsaturated digalacturonic acid from the reducing end of pectic acid by a terminally acting polygalacturonic acid *trans*-eliminase[87].

Screening of several species of the genus *Corynebacterium* did not bring out presence there of polygalacturonase or pectin methyl esterase. Similarly, no pectic enzymes were demonstrated in a pathogenic culture of *Corynebacterium* sp., viz. *C. sepedonicum* growing on synthetic media containing various pectic substances[88]. However, later investigations on non-pathogenic species have indicated the presence of pectinolytic enzymes in the genus[55,76,80]. Significantly, *C. barkeri* isolated from sewage was found to possess the enzyme *trans*-eliminase[55,89].

Pectinolytic enzymes have also been demonstrated in aerobic bacteria belonging to the genera *Micrococcus*[55,84,90] and *Arthrobacter*[84]. The organisms in this case were isolated from the rets of sisal and coconut husk.

Among the aerobic bacteria, pectinolytic property is widespread among the species in the genus *Bacillus*. Nortje and Vaughn[91] studied the pectinolytic properties of 43 aerobic spore forming bacteria isolated from the brines of normal and softened cucumbers and olives. Twenty-one of these were

identified as cultures of *B. subtilis* and 22 as *B. pumilus*, and all were pectinolytic in so far as they could bring about the softening of olives and pickles. Cultures of *B. pumilus* and *B. circulans* isolated from fermenting tobacco were found to elaborate polygalacturonase but not pectin methyl esterase[92]. A polygalacturonase-like enzyme has been demonstrated in *B. mesentericus*[86].

In recent years, considerable attention has been paid to the pectinolytic activity of *B. polymyxa*. Smith[81] observed polygalacturonase production by six cultures including two strains of *B. polymyxa*. While investigating the pectic enzymes of *B. polymyxa*, Nagel[93] observed an altered digalacturonic acid differing from the normal compound in its rate of migration on paper chromatogram as well as in its rate of cleavage by tomato polygalacturonase. The factors affecting growth and enzyme secretion by this organism have since been elaborately studied by Nagel and Vaughn[46-48] and the enzyme *trans*-eliminase was shown to be the one responsible for the cleavage of the glycosidic linkages. Recently, the action of this enzyme in *B. polymyxa* was followed using normal and oligogalacturonic acids as the substrates[94].

More recent evidence furnished by Dave and Vaughn[95] suggests that in contrast to the other polygalacturonic acid *trans*-eliminase studied, the enzyme of *B. pumilus* produces a large quantity of unsaturated trigalacturonic acid.

Yeasts

The ability to utilize pectin is not as widespread among the yeasts[80,96-98] as in bacteria. At the same time available information indicates that, although yeasts as a class cannot be regarded as efficient in their action on pectin, they do contain a few species which are highly active and which hold promise of their utilization in the industry. Luh and Phaff[97,99,100] were the first to throw light on the depolymerase type of polygalacturonase in yeasts. An examination of 181 yeast cultures representing several genera revealed pectinolytic activity in only six of them. Similarly, Bell and Etchells[101] found that only 6 of the 139 yeast cultures representing 61 species in 15 genera could bring about a glycosidic hydrolysis of the pectin molecule. These workers further observed the de-esterification of the pectin cultures of 20 species in the genera *Candida, Debaryomyces, Endomycopsis, Hansenula, Rhodotorula* and *Zygopichia*. However, according to Bell and Etchells[101], the method employed for the assay of the enzyme pectin methyl esterase is not satisfactory.

While referring to the pectinolytic activity among yeasts, mention may be made of Wieringa[102] who pointed out the role of *Pullularia pullulans* in pectinolysis but was unable to detect it in *Cryptococcus laurentii*. Bilimoria and Bhat[103], however, succeeded in demonstrating pectinolysis in a culture thereof under suitable cultural conditions. This culture was of marine origin. Hydrolysis of pectin by certain other salt-tolerant yeasts has also been achieved[80,103]. Among others, Corrao[96] detected pectinolytic activity in a culture of *Saccharomyces ellipsoideus* and Phaff and Demain[104] in *S. fragilis*. They prepared the enzyme polygalacturonase from *S. fragilis* and established the enzyme as constitutive preferring pectic acid to pectin as substrate and capable of degrading di-, tri- and tetra-galacturonic acids but not other oligouronides. Of 166 strains of yeasts isolated from grapemust, Malan[105] found 44 strains of Saccharomyces to possess hydrolytic activity on pectin. Roelfsen[4] examined the yeasts isolated from fermenting cocoa beans in Java and reached the conclusion that yeasts produced polygalacturonase and that the degree of maceration of collenchyma tissue of the beans was dependent on the quantity of enzymes elaborated.

Vaughn[83] and Vaughn *et al.*[106] reported in *Rhodotorula glutinis* (a pink yeast) and *Saccharomyces fragilis* the presence of polygalacturonase and pectin methyl esterase but not *trans*-eliminase. Supporting evidence in favour of this view was provided from this laboratory with *Saccharomyces marxianus, S. bayanus* and *S. cerevisiae* var. *ellipsoideus* isolated from fermenting coffee beans[9,56]. Frederiksen[68,107] succeeded in the isolation of pectinolytic yeasts from dew retted flax. One of them, *Rhodotorula macerans*, besides being pectinolytic, produced carotenoids and starch. The pectinolytic yeasts encountered in the rets of coconut husk were identified to be *Cryptococcus diffluens, Rhodotorula glutinis* and *R. flava*[84].

Actinomycetes

Even the more recent and excellent reviews on pectic substances and pectic enzymes have provided only scanty information on actinomycetes decomposing pectin. Waksman[108] was the first to suggest that " Actinomycetes may prove to be the most useful tools for the preparation of pectinolytic enzymes ". Likewise, Wieringa[109], devising a method for the isolation and enumeration of pectinolytic anaerobes, observed a comparatively higher incidence of actinomycetes in certain samples of soil and suggested a probable role for them in the natural decomposition of pectic substances. The assumption was proved correct in the detailed examination carried out in this laboratory on Streptomyces[55,80,110]. Evidence was adduced to show that actinomycetes in general and *S. viridochromogenes* species in particular are perhaps the most potent of the organisms from the point of view of pectinolytic enzyme synthesis[80,110]. Of more than ordinary interest were the observations that (i) a large majority of streptomycete cultures stored in the laboratory over years on nutrient agar were pectinolytic even in the first transfers in pectin containing media, and (ii) the actinomycetal preparation had its optimal activity in the alkaline *p*H range.

Making use of the method of Wieringa[109], Kaiser[111] reported the isolation of pectinolytic actinomycetes. A polygalacturonase was subsequently demonstrated in *Streptomyces glaucus* and *S. oidiosporus* isolated from canned fruits[112]. The search for pectinolytic actinomyces, in this context, resulted in the devising of a preferential method[113] for the selective isolation of actinomycetes from various environs. This technique, termed as 'high temperature preincubation' method, yielded a good majority of

actinomycetes from a mixed population. What is more significant is that the species isolated were pectinolytic and stored soils were found to yield significantly higher yields of actinomycetes than freshly collected soils[114]. Many species of Streptomyces, freshly isolated or otherwise, were observed to possess the enzyme *trans*-eliminase[55,115].

Protozoa

Though cellulolytic, diastatic and proteolytic activities of a variety of protozoal species have been studied in detail, attention worth a mention has not been paid to ascertain the nature and distribution of pectinolytic enzymes in these animalcules. Wright[116,117] was perhaps the first to show the existence of pectinolytic enzymes in a mixed protozoal population of the bovine rumen. Subsequently, several rumen protozoa, as *Entodinium caudatum, Dasytricha ruminantium, Isotricha* sp., *Ophryosedex caudatus, O. purkynei,* and *Polyplastron multivesiculatum* were reported to be pectinolytic by several investigators[118-121]. Protozoa from other environs, however, remained uninvestigated from this viewpoint until a chance finding in this laboratory pointed to the vital role they have in the retting of plant fibres[80]. Concerted attempts since then have indicated the ciliates from *Calotropis* rets, identified as *Plagiopyla* sp., as those able to produce considerable amounts of pectinolytic enzymes, viz. polygalacturonase, pectin methyl esterase and *trans*-eliminase[55]. Stalked ciliates identified as species of *Vorticella, Epistylis* and *Carchesium* associated with the aerobic stabilization of waste waters were also shown to be pectinolytic[55,56,122].

Fungi

Extensive literature on the pectinolytic ability of fungi has accumulated mainly because of the significance of this group as plant pathogens and to a lesser extent due to the ability of some of the members to function as suitable organisms in industrial fermentations.

Penicillium species were found to secrete potent pectinolytic enzymes on the jute bark but the extent of activity of each of the different enzymes, viz. polygalacturonase, pectin methyl esterase, and protopectinase, was found to differ in the same culture. The feasibility of employing pectin methyl esterase and protopectinase obtained from species of *Aspergillus* and *Penicillium* on the retting of jute was explored in this context and the relative merits and demerits of the different enzymes on bringing a successful completion of retting were compared[123]. Determination of the activity of pectic enzymes in extracts from sound apples and from those attacked by *Penicillium expansum* led to the finding that the extracts from the rotten samples had a very high polygalacturonase and pectin methyl esterase activity[124]. Culture fluid of the organism liberated galacturonic acid from apple fruit fibre, thereby presenting a positive proof for the presence of pectinolytic enzymes in the *Penicillium*. Likewise, the attempts made by Tuttobello and Mill[125] for the preparation of a mixture of pectinolytic enzymes from *A. niger* yielded a 400-fold purified material with 34 per cent recovery. The stability of the enzymes and their relative ability to degrade different pectic substances were then ascertained.

The oxidation products of leucoanthocyanins were tried as inhibitors of fungal polygalacturonase produced by *Schlerotinia fructigera* causing apple rot and it was observed that the phenolic substances inhibited the action of pectinolytic enzymes in the rotted apple[126]. This is an interesting observation in the context of the time needed for the retting of coconut husk coated, as it were, with phenolic compounds or in the context of other discoveries subsequently made on the subject[127,128,84].

Other fungi tested for their pectinolytic activity were *S. fructigera* and *S. laxa* and measurements for their activity were made by methods involving maceration of plant tissues, viscosity reducing determination in pectic substrates and increase in acidity of pectin[129]. Both the species produced pectinolytic enzymes in synthetic media as well. Of interest was the observation that with *S. fructigera* the formation of pectinolytic enzymes[130] increased when glucose was replaced by pectin in the medium. Also, the extracts of apple rotted by *S. fructigera* had little or no polygalacturonase activity though they possessed intense pectin-esterase activity[124]. Evidence was presented by Reinganum[130] in favour of fungal pectinolytic products providing suitable carbon sources for the *in vivo* growth of *S. fructicola* and in relation to the carbohydrate requirements of this pathogenic species.

The factors affecting the production of protopectinase by *Rhizoctonia solani* and other species of the genus were investigated[131]. Two assay methods for polygalacturonase were developed and the presence thereof in *R. solani* isolated from damped off seedlings established. Results of the studies were suggestive of the enzyme acting differently on different substrates and comprised possibly two separate enzymes[132]. The pectinolytic activities of culture filtrates of *R. solani* and extracts of *Rhizoctonia* infected tissues of bean were comparable with respect to reduction in viscosity of sodium polypectate but differed with respect to liberation of reducing group[133]. Thermal inactivation studies of polygalacturonase from both sources at different *p*H levels indicated that the enzyme systems were indeed different. The growth and pectic enzyme production by three *Rhizoctonia* strains isolated as *Mycorrhizae endophytis* from orchid roots and two pathogenic *R. solani* strains from potato and rice were investigated[134]. Pectin was a less efficient carbon source for growth than glucose though it promoted secretions of large amounts of pectinolytic enzymes.

With a view to gaining an insight into the physiology of parasitism, the killing of cucumber and turnip tissue cells by *Botrytis cinerea* and *Bacterium aerodicae* was compared in the presence of plasmolysing concentrations of various alkaloids[135]. Evidence was adduced to show that the enzyme system which macerated the host wall was responsible for bringing about the death of the protoplasts. The chocolate spot disease of beans (*Vicia faba* L.) caused by *Bacterium fabae* was generally believed to be the result of the interaction of polygalacturonase systems of the

fungus and the phenolase system of the host. The findings leave little doubt about the interrelationship between phenolase activity of the bean leaves and the pectinolytic-cellulolytic activity of the invading organisms[136]. The mechanism by which the fungi cause the lesions was also worked out; a study on apples rotted by *B. ribis and P. italicum* brought into focus the occurrence of a variety of enzymes including pectinolytic ones in the hydrolysed cell wall polysaccharides of the fruit.

The relative activity of polygalacturonase, pectinase and protopectinase in *Botrytis cinerea, B. tulipae, B. allic* and *B. anthophila* was evaluated[137]. Maximum activity was observed to develop in glucose medium. Introduction of pectin into the medium only slightly increased the activity of the enzymes. A highly active pectinase was found to be produced during the germination of uredospores of *Puccinia triticina, P. glumarum, P. suavesleus* and *Phragmidium mucronatum*[137]. The pectinolytic activity of the germinating spores of Botrytis and *A. niger* exceeded by several folds the pectinolytic activity of the mycelia.

Each of the anthracnose fungal isolates of *Glomciella cingulata, G. magna* and *G. lagenaria* formed pectinolytic enzymes capable of hydrolysing pectin and sodium polypectate gel[138]. Maximum polygalacturonase was obtained from culture fluids of the fungi grown in pectin and the peak activity was demonstrable when the organisms had attained a minimum dry mycelial weight of 40 mg. Unlike *Glomciella* species the strains of *Coniophora carebella* secreted pectinolytic enzymes of high activity in the presence of galacturonic acid, pectic acid or pectin[139]. No difference in properties was observed between the extracellular and intracellular enzymes, although the former was superior in its activity.

Investigations on 40 strains of *Verticillium* belonging to the species *Verticillium alboratrum, V. tricorpus, V. dahline, V. nigrescens, V. lateritium* and *V. hemileiae* brought to light the high pectinolytic activity prevalent in all these pathogenic species and its absence in the non-pathogenic counterparts[140]. Subsequent work of Blackhurst and Wood[141] showed that the secretion of polygalacturonase by virulent *Verticillium alboratrum* was greatly stimulated by pectic substances and organic nitrogen sources rather than by sources of inorganic nitrogen. Degradation of pectate by this enzyme was, however, limited to 25 per cent hydrolysis of the glycosidic linkages.

That the extent of mycelial growth need not necessarily influence production of pectinolytic enzymes was shown in a study designed to find the effect of various cultural conditions for the optimal production of enzymes by the plant pathogenic *Pythium debaryanum.* It is interesting to record that the pectic enzymes of potato soft rot causing organisms, *P. debaryanum, E. aroideae* and *B. cinerea,* are devoid of polygalacturonase or pectin esterase activity[142].

The *in vivo* detection of pectin methyl esterase in *Fusarium* wilt of cotton and its formation was worked out by Lakshminarayana[143]. The enzyme protopectinase was partially purified by precipitation in 60 per cent acetone at *p*H 6·0 from the culture fluids of *F. moniliforme*[129]. Chromatographic evidence indicated that the pectate and pectin were degraded in different ways. Although the pathogen *F. moniliforme* secreted protopectinase, it could not parasitize potato tubers in contrast to *F. abenacium* which readily attacked potato tubers devoid of the enzyme protopectinase[129].

Studies on the synthesis of pectic enzyme in relation to virulence of *F. oxysporum* indicated that the virulent strains grew better and produced more pectic enzymes than the avirulent strains[144]. Such a difference became more pronounced in media with high pectin content and at an enhanced temperature of incubation raised from 15° to 28°C. The investigations of Mann[145] on mutants of *F. oxysporum* unable to produce extracellular pectic enzymes indicated that the ability to produce the enzymes was not essential for the development of wilt symptoms. Evidence was adduced to show the ability of the mutants to elaborate pectin methyl esterase but no correlation was found between the *in vitro* ability to produce the enzymes and pathogenicity[146]. Pectin depolymerase was secreted in larger quantities by the pectin preadapted fungus grown on susceptible tissues than by fungus preadapted to glucose[147]. Susceptibility to fusarium wilt of tomato is correlated with a large increase in pectin depolymerase activity in susceptible plants[148].

Ragheb and Fabian[149] found pectinolytic activity at varying *p*H levels in 25 moulds of different genera isolated from tomato plant. Analysis of the commercial cucumbers salt-stock brines yielded 99 Gram positive spore forming bacteria and 15 yeasts, but none of them revealed any pectinolytic activity under stimulated commercial conditions; 10 genera of filamentous fungi isolated, on the other hand, were highly to moderately pectinolytic under identical conditions[83]. All produced polygalacturonase but not methyl esterase. It was also pointed out by Ragheb and Fabian[149] that pectin methyl esterase found in the pickling vats was elaborated from cucumbers. In fact, it was concluded that both cucumbers and the fungi were responsible for the pectinolytic softening of cucumbers observed under commercial salt-stock conditions.

Recently, Edstrom and Phaff[53,54] screened several fungi of the genus *Aspergillus* for the presence of the newly discovered enzyme pectin *trans*-eliminase and successfully purified the enzyme from the culture fluid of *A. fonsecaeus.* They showed the specificity of this fungal *trans*-eliminase for pectin in which respect it differed from the polygalacturonic acid *trans*-eliminase of bacterial origin. The effects of *p*H, cations and a few anions on the activity of the enzyme also were reported. The course of action of *A. fonsecaeus* pectin *trans*-eliminase on pectin and on certain oligogalacturonide methyl esters was followed and the products of these reactions were analysed. However, subsequent investigations of fungal *trans*-eliminase indicated a polygalacturonic acid *trans*-eliminase activity in alfalfa leaves infected with certain pathogenic fungi[150]. Whereas *Colletotrichum trifolli* yields extremely high *trans*-eliminase activity, much lower activity is associated with alfalfa leaves infected

with *Stemphylium botrycoum*. No activity is found in *Ascochyta* infected leaves.

Conclusion

Though several groups of microorganisms possess the ability to elaborate pectinolytic enzymes, the beneficial influence or otherwise of these enzymes either on the microorganisms or the ecosystems in which they exist differs distinctly. The different types of microbial pectinolytic enzyme systems might be exploited at a future date as useful tools in the elucidation of their mechanism of action on different pectic substrates. Such an investigation, although fundamental, is of great practical significance in view of the involvement of pectic substances in several commercial problems. Though concerted attempts in this direction show positive trends and signs, much of the confusion prevailing at the moment is attributable to the lack of knowledge on the exact chemical composition of these substances. A comparative study of the action of various microbial systems on pectic substances alone will bring order into the chaos existing in the field of pectic substances and pectinolytic enzymes.

Summary

The review deals with the chemistry and utility of pectic substances and discusses the nature and characteristics of the enzymes catalysing the degradation of pectic substances. Attempts made at classification of the enzymes as well as detection of products of pectin degradation are referred to along with the manner in which the molecules get broken.

The bacteria, yeasts, moulds, actinomycetes and protozoa associated with the process of pectin degradation are listed and their activities are given. The relative significance or otherwise of the various microorganisms in the process is discussed. The available information on the distribution of different pectinolytic enzymes among microorganisms in particular and some of the plant material in general is presented. The role of investigations on pectin degradation in the understanding of their chemistry and microbiology is indicated.

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REVIEWS

THE DECIBEL NOTATION by V. V. L. Rao (Asia Publishing House, Bombay), 1967. Pp. xxiv+211. Price Rs 20.00

The volume under review is the second edition of a book first published by the author in 1944 which undoubtedly fulfilled a definite want in the technical literature on radio engineering and acoustics. The decibel is a unit of measurement most widely used in the fields of telecommunication and electro-acoustics. One may naturally wonder as to how a book simply on a unit of measurement be written. But as he goes through the pages of the book it will be realized that there is much to learn about this simple unit and its significance in a wide variety of applications in the above fields. It is the object of this book to explain the origin, development and a wide range of applications of this notation, with special reference to radio engineering and acoustics, illustrated by a number of worked out examples, as well as to give a clear picture of the justification of the use of the decibel notation.

The book comprises three major chapters and five appendices. The first chapter gives a summary of the origin, development and the meaning of the decibel notation. The second chapter discusses the decibel levels of acoustics, the derivation of the Phon notation of sound engineering and the use of the decibel notation in the assessment of acoustical noise. The final chapter deals with the applications of the decibel notation to radio engineering and acoustics including VHF broadcasting, sound broadcasting, waveguide and coaxial cables, radar transmitters and receivers, radio transmitters and receivers, transistors, and transmission lines and feeders. Moreover, the five valuable appendices include discussion relating to the types of graphs used in radio engineering and acoustics, the limitations of a logarithmic unit and the use of log tables.

The book does not use high standard mathematics and as such can be followed by an average student of electrical engineering. The subject has been developed in this monograph from the first principles wherever possible. The style is clear and lively and the exposition is concise. The index and the bibliography appear to be adequate. The material presented in the text should be of considerable interest to anyone active in the fields of telecommunication and sound engineering.

A. N. CHAKRAVARTI

SELECTED PAPERS OF GEORGE HEVESY (Pergamon Press Ltd, Oxford), 1967. Pp. ix+447. Price 90s.

This is an abridged version of *Adventures in radio-isotope research* printed earlier by the publishers during the lifetime of this great scientist. A rare investigator, blessed with the gift of turning everything he touched into contributions of significance, Prof. George Hevesy made important discoveries, one after another. This collection of fifty-one selected papers is illustrative of the author's wide interests ranging from inorganic chemistry to biology as well as his pioneering contributions to the science of nuclear medicine. The comments added at the end of each series of papers, classified topic-wise, amplify the significance of his studies.

The papers are presented chronologically, starting with early explorations in inorganic and physical chemistry (papers 1-9) which have offered effective tools for chemical and biochemical procedures. Thus, determination of lead content of rocks led to the 'isotope dilution technique'. The recognition of radioactive indicators opened up the field of 'activation analysis' and resulted in the discovery of hafnium.

The therapeutic uses of the salts of bismuth, lead, etc., led to enquiries on the distribution of these unusual elements in the animal body. In fact, this could be considered as the first application of radioactive tracers in animal physiology (papers 10-16). Production of radioactivity by neutron bombardment gave rise to another significant isotope, that of phosphorus (^{32}P), which revolutionized concepts in biochemistry, indicating the highly dynamic situation that prevails in the living organism. With ^{32}P and ^{45}Ca, it was shown that even the skeleton gets renewed. The author studied in considerable detail the formation, turnover and metabolic implications of phosphorus compounds (papers 17-23), including nucleic acids (papers 36-41). Water content in the human body and the significance of ion transport did not escape the attention of Prof. Hevesy. While extending the techniques of Schoenheimer and Rittenberg using deuterium, the author exploited the isotopes of sodium, potassium, chlorine, bromine, thorium and iron (papers 25-35). Similarly, heavy and radioactive isotopes of carbon were employed to study turnover of fatty acids in mouse liver (paper 24).

In later years, Prof. Hevesy's interests were drawn towards radiation biology with particular reference to blood cancer (papers 42-45), to pointing out the abnormalities observed in the distribution of iron in tissues and blood, and that of phosphorus in nucleic acids. Using tissue culture technique, it was pointed out that though X-rays caused mitotic arrest, DNA synthesis could still go on, independent of cell division mechanisms. The last section (papers 46-51) essentially describes how isotope tracer procedure was extended to investigations in plant physiology.

This catalogue of collected papers would make a good addition to the archives of science.

G.B.N. & A.S.

PHOTOCHEMISTRY AND REACTION KINETICS edited by P. G. Ashmore, F. S. Dainton & T. M. Sugden (Cambridge University Press, London), 1967. Pp. 378. Price 75s.

The book, dedicated to Ronald George Wreyford Norrish in commemoration of his valuable scientific contributions in the broad fields of reaction kinetics

and photochemistry, contains twelve valuable chapters dealing with various aspects in which Prof. Norrish has done pioneering work. The articles have been contributed by his admiring former students and colleagues in UK and by three eminent people in USA and USSR with scientific interests in fields in which Prof. Norrish has blazed new trails and has made signal contributions for over half a century now. Prefaced with a note on Prof. Norrish's scientific interests by Dainton, the twelve chapters — viz. (1) Contributions of R. G. W. Norrish to photochemistry by W. A. Noyes (Jr); (2) Contributions of R. G. W. Norrish to combustion by Bernard Lewis; (3) Photochemistry in the liquid phase by C. H. Bamford and R. P. Wayn; (4) Gaseous photochlorination by F. S. Dainton and P. B. Ayscough; (5) Flash photolysis by George Porter; (6) Flash photolytic studies of free radicals in the gas phase by B. A. Thrush; (7) Energy transfer in molecular collisions by A. B. Collear; (8) Polymer chemistry by J. C. Bevington; (9) Modern concepts of the mechanism of hydrocarbon oxidation in the gas phase by N. N. Seminov; (10) The interpretation of cool flame and low temperature combustion phenomena by John H. Knox; (11) The sensitization and inhibition of ignitions by P. G. Ashmore; and (12) The pyrolysis of paraffins by J. H. Purnell and C. P. Quinn — make extensive references to Prof. Norrish's contributions and make a very interesting reading. Every chapter reveals that much of our fundamental knowledge — be it on oxidation, combustion, photolysis, polymerization, ignition, etc. — is a result of systematic and painstaking experimental work by Norrish's school. That his contributions in photochemistry in the liquid phase have been equally spectacular is revealed in this book.

The chapters contain information highly technical in their contents and very useful for research workers in the related fields. The book is free from printer's devils, mistakes of minor or major nature. The reviewer has, however, only one disappointment and that is with regard to the timing in bringing out this book and its size. So vast and extensive are the scientific contributions of Prof. Norrish that had this book been brought out after he was awarded the Nobel prize in chemistry and included many more interesting articles from eminent people from all parts of the world, it would have been a more fitting tribute to the stupendous and amazing scientific activity of Prof. Norrish.

M. SANTAPPA

DESIGN OF BYPRODUCT RECOVERY UNITS OF COKE PLANTS by I. E. Korobchanskii & M. D. Kuznetsov, translated from the Russian by S. Sarkar (Asia Publishing House, Bombay), 1968. Pp. viii+293. Price Rs 28.00

Basic design considerations for byproduct recovery, as practised in the case of high temperature carbonization of coals in the conventional commercial coke ovens, have been taken into account in detail in this book. As the pattern of byproducts varies both in quality and quantity for low and medium temperature carbonization and is likely to be different in the case of high temperature carbonization, if performed in equipment other than coke ovens, certain alterations in such cases may be necessary in design of equipment. However, the book will be of immense help to the designers, operating and maintenance personnel in the coke oven byproduct plants, besides acting as a regular guide to students of fuel technology and chemical engineering.

The book is divided into three parts. Part I deals with direct and indirect types of primary coolers for coke oven gas (Chapters 1 & 2). Part II describes treatment of liquor and its dephenolization (Chapter 3); production of ammonium sulphate (Chapter 4); and recovery of pyridine bases from saturator-mother liquor (Chapter 5). In Part III, matters relating to final cooling of coke oven gas (Chapter 6) and recovery and production of raw benzol (Chapters 7 & 8) have been discussed. In each chapter a short description of technological flowsheet, construction and working principle of the main equipment and their design features have been presented. The value of the book is remarkably enhanced by the inclusion of 36 figures and 12 tables. A 45-page appendix presents physico-chemical constants, valuable design data (in 48 tables) and useful equations.

The treatment of the subject is based on fundamental principles and the calculations for both process and equipment design have been presented in great detail. All units having been designed for one plant, there is a remarkable continuity in the treatment from one unit to another and yet the readers would find no difficulty in pursuing calculations for an individual unit of their choice. Where more than one type of unit is in use, the book gives the design of the important types. Thus, for instance, both the direct and indirect types of tubular primary coolers are given exhaustive consideration.

Fuel technologists and chemical engineers will like this book from the standpoint of equipment design which is an important aspect of their subjects. Students as well as professionals will find in this book a number of examples worked out for diverse types of equipment for heat and mass transfer. Many of these examples relate to complex situations and are not amenable to simple solution. Readers, both beginners and specialists in the field, will find some new approach in the design of coolers, absorbers, heat exchangers, etc. Some minor printing errors have, however, been noticed in the text as well as in some of the figures.

Himself engaged in teaching fuel technology at a higher technological institute in India, the translator, Dr Sarkar, has presented a useful English version of the unique book in Russian by the late Prof. Korobchanskii, Head of the Department of Fuel Technology, Donetsk Polytechnic Institute of Dnepropetrov, USSR, and his able successor Prof. Kuznetsov. Dr Sarkar's brief annotation on page v will be helpful to the readers. He has taken pains to convert all the symbols into convenient forms for the benefit of the readers. The book is a welcome addition to the technical literature on coal carbonization and equipment design.

K. Y. SHRIKHANDE

THE MILLIPEDE — THYROPYGUS (CSIR Zoological Memoir No. 1) by G. Krishnan (Council of Scientific & Industrial Research, New Delhi), 1968. Pp. 84. Price Rs 12.00

Valuable research in various zoological fields has been carried out in India, and the results of these investigations lie scattered in numerous Indian and foreign scientific periodicals. The need for stringing together this information has long been felt. To achieve this end, two series of publications were envisaged by CSIR: (i) Memoirs on Indian animal types to serve as guides for students and teachers in the universities and (ii) Monographs on selected subjects of special interest to postgraduate students and research workers. Specialists have been invited to write the selected topics for both the series.

The millipede is prescribed as one of the animal types for study by the B.Sc. students in most of the Indian universities, and there has always been a need for an exhaustive account of some common Indian species of millipedes. In this well-illustrated memoir, ten species of millipedes, belonging to the genus *Thyropygus*, have been dealt with together with their distribution. The major portion of the introduction is devoted to the classification of diplopods with reference to systematic position of *Thyropygus*. *T. poseidon* Attems is described in detail, the account covering the following aspects: (i) External features; (ii) Integument; (iii) Skeleto-muscular system; (iv) Alimentary canal; (v) Blood-vascular system; (vi) Excretory organs; (vii) Fat body; (viii) Repugnatorial glands; (ix) Nervous system; (x) Sense organs; (xi) Neuro-secretory system; (xii) Reproductive system; (xiii) Larval development; (xiv) Water relations; (xv) Habit and habitat; and (xvi) Affinities. In keeping with the modern trends in zoological studies, emphasis has been laid not only on anatomical details, but also on ecological and physiological aspects correlated with the structure. A detailed account of cuticle is of special significance. Instructions for practical work are provided which make the publication especially useful to graduate students.

The book, written by Dr G. Krishnan, Director, Zoological Research Laboratory, Madras University, Madras, a specialist in the field of anthropod anatomy, presents information in a lucid and easy-to-grasp form. It is a valuable addition to the zoological publications published in India, and is indispensable for students, teachers and research workers.

FERTILIZATION: COMPARATIVE MORPHOLOGY, BIOCHEMISTRY AND IMMUNOLOGY: Vol. I, edited by C. B. Metz & A. Monroy (Academic Press Inc., New York), 1967. Pp. xiii+489. Price $ 22.00

Current preoccupation in stemming the tidal waves of population upsurge has rekindled academic interest in the basic mechanisms of reproduction, particularly those which may be susceptible to interruption by designed chemical or biomechanical techniques for planned limitation of fertility. It hardly needs reiteration that fertilization is a most fundamental event in reproduction and indeed a property of living systems. Accordingly, it is in the fitness of things that research in biology, biochemistry and control of fertilization process continues to be an area of multi-disciplinary interest.

A voluminous body of information on fertilization has accumulated over years and the present treatise has attempted to bring the extant knowledge and ideas on certain aspects of this phenomenon within its compass. These include: (i) problems and procedures of comparative gametology and syngamy; (ii) sperm motility; (iii) sperm metabolism; (iv) mechanism of gametic approach in plants; (v) gamete surface components and their role in fertilization; (vi) acrosome reactions and lysins; (vii) membrane fusion in relation to sperm-egg association; (viii) the activation of the egg; and (ix) parthenogenesis in vertebrates. Each topic is written by an expert who has made special effort to ensure that the presentation is adequate in scope and amplitude for biologists, research workers and teachers alike.

The most commendable feature of the treatise is that it is not a mere catalogue of facts or a conventional review of the literature; rather it is a critical evaluation of existing data and views, presented in a form that will serve as direction-pointer for new avenues of research. An additional impact is likely to be a stimulation of interest in comparative study of reproduction phenomena in different organisms, from the simplest to the most highly differentiated, covering morphological, physiological, chemical and physical aspects.

The printing and format are excellent, and the illustrations superb. The editors and the Academic Press are to be congratulated for this meritorious and timely publication.

A. B. KAR

THE BIOCHEMISTRY AND PHYSIOLOGY OF INFECTIOUS PLANT DISEASE by R. N. Goodman, Z. Király & M. Zaitlin (D. Van Nostrand Co. Inc., Princeton), 1967. Pp. x+354. Price $ 12.50

Plant pathology has been passing through at least two distinct phases in this century. With an almost exclusive symptomatology phase it has gradually entered one of critical appraisal of cause and effect. Here, borderline researches on the impact of biochemistry and plant physiology in understanding the mechanisms leading to deranged host physiology, consequent on pathogenesis, have yielded rich dividends. The book under review is a notable and concerted effort of three specialists in two continents who have brought to bear their own researches and the achievements of many others on this fascinating field of enquiry. The result is a clearly written first ever attempt to collate and interpret all that is worth knowing in the area of the dynamics of host-parasite interaction.

Quite obviously, much background knowledge is necessary to understand the many intricacies of deranged physiology. The authors have carefully chosen these areas which include photosynthesis, respiration, nitrogen metabolism and growth. To introduce the subject against basic plant physiology, therefore, is not only very necessary but also of immense advantage to those who are to be initiated into this new field of study. Literature coverage has been as extensive as possible commensurate with the size of the volume now before us. Areas of special interest in recent years such as phenol metabolism, growth regulator metabolism and toxin

induced changes in host physiology have been given adequate coverage.

Much of what this subject is today is due to the pioneering work of plant virologists. The most challenging areas still exist in this field; viral synthesis *in vivo* has yet to be completely understood, especially plant-virus nucleic acid synthesis. Vascular transport and its derangement, ionic imbalance in the wake of pathogenesis, pectic enzymes in disease, loss in integrity of the cell wall and its consequent repercussion on metabolism are all adequately covered. The newly emerging field of isolating and characterizing abnormal substances collectively called phytoalexins, which are currently considered to constitute the first line of defence in plants under pathogenesis, is very well presented and constitutes a new approach in considering biochemical aspects of deranged metabolism. For the researcher this area is a very challenging one. The questions frequently posed are: 'Is there a defence mechanism in plants? Do plants form antibodies *in vivo*?'

The book is written in a pleasing and clear style with select bibliography and meaningful illustrations. There are some printing lapses here and there but not of much consequence. The book is written for the specialist and should attract the attention of fundamental biochemists and plant physiologists who are unaware of how much has gone in this field of 'stress physiology and deranged host metabolism' and how much more awaits expert attention. However, the discerning student who wishes to specialize in plant pathology after a course in virology, mycology or bacteriology will find this book invaluable as it summarizes much new knowledge on the metabolism of diseased plants currently available. I have been stimulated by reading through and I strongly commend the book for serious study by all those interested in this new area of research.

T. S. SADASIVAN

WORK DONE IN INDIA ON VIRAL AND RICKETTSIAL INFECTIONS OF VERTEBRATES — A BIBLIOGRAPHY (Indian National Scientific Documentation Centre, New Delhi), 1967. Pp. xii+339. Price Rs 50.00, £ 10 or $ 30.00

In any medical library, bibliographies of publications on diseases are comparatively rare. This is mainly because of the tremendous amount of painstaking work of technical nature involved in their preparation. Virology as a subject is comparatively new, and viral infections have been dealt with as a separate entity rather recently. These facts, however, do not minimize the immensity of the task of preparing this bibliography because earlier works, now known to belong to the domain of virology, had to be combed out of the vast amount of clinical, therapeutic and bacteriological data.

The scope of this bibliography, the first of its kind in India, extends from 1900 to 1964. It falls into two broad divisions, one relating to man and the other to animals and birds. There are altogether 3267 entries in this publication, of which 2223 are taken up by viral infections in man, 644 by viral infections in animals and birds, 226 by rickettsial infection in man and 16 by rickettsial infection in animals. There are also 120 entries on bacteriophage and 38 on vectors. In general, the classifications of Sir Christopher Andrews in his classical work *Viruses of Vertebrate* have been adopted. When dealing with each disease, a broad division has been made into virus study and virus infection. Each of these two has been subdivided further, and in the ultimate subject the entries are arranged chronologically. Wherever there are synonyms, they have been indicated within brackets.

A 12-page introduction contributed by Dr T. Ramachandra Rao, whose inspiration and guidance were at the back of this publication, traces the history of viral and rickettsial research in this country. While giving an excellent summary of all the important works carried out, it reveals that Indian medical and veterinary research workers have not lagged much behind those of other countries.

The book deserves a place on the shelf of any scientific worker interested in virus research and in all the medical libraries in the country. The compilers, under the able guidance of the Director, INSDOC, deserve all credits for providing such a documentary which will be of immense relief to anyone searching for references of any virological work carried out in India.

J. K. SARKAR

PUBLICATIONS RECEIVED

PRINCIPAL FUNCTIONS by Burton Rodin & Leo Sario (D. Van Nostrand Co. Inc., Princeton), 1968. Pp. xviii+347. Price $ 10.50

MODERN FLUID DYNAMICS: Vol. 1 — INCOMPRESSIBLE FLOW by N. Curley & H. J. Davis (D. Van Nostrand Co. Inc., Princeton), 1968. Pp. xiv +290. Price $ 5.95

THE PHYSIOLOGICAL CLOCK by Erwin Bünning (Longmans, Green & Co. Ltd, London), 1967. Pp. 167. Price 24s.

ANALYSIS OF INDETERMINATE FRAMEWORKS by N. M. Thadani (Orient Longmans Ltd, Bombay), 1967. Pp. 266. Price Rs 25.00

THE IDENTIFICATION OF VAT DYES ON CELLULOSIC MATERIALS by D. A. Derrett-Smith & J. Gray (Pergamon Press Ltd, Oxford), 1967. Pp. v +113. Price 35s.

ISOTOPES IN RESEARCH AND PRODUCTION — TECHNICAL FUNDAMENTALS, translated from the German by Herbert Liebscher (Asia Publishing House, Bombay), 1967. Pp. 126

NOTES & NEWS

Evidence of a new particle

An experiment conducted on cosmic-ray muons by University of Utah scientists, 1850 ft underground in a mine in Utah, has yielded evidence for the possible existence of the intermediate bason, a particle postulated by theoretical physicists a few years ago as the agent responsible for the radioactive, or ' weak ', interactions [*Phys. Rev. Lett.*, **19** (1967), 1487].

The cosmic-ray muons are generally supposed to be the decay products of the mesons known as pions and kaons. The present experiment has, however, yielded results which are in contradiction to this accepted fact. In the experiment, the intensity of cosmic-ray muons was measured as a function of depth and zenith angles. At a given zenith angle, excellent agreement with the currently accepted dependence of intensity on depth has been established. However, the absence of any variation in intensity with zenith angle strongly contradicts the theory that these muons are derived from pions and kaons. This along with certain other observations have led to the conclusion that the majority of cosmic-ray muons of energy greater than 10^{12} eV. are produced either directly or as the progeny of a parent which decays copiously into muons with a mean life much shorter than that of the kaon. It is a matter of speculation, till further sophisticated experimentation is carried out, whether the ' parent ' is the intermediate boson, but the unexpected results of the Utah experiment may lead to a new break-through in particle physics.

Static extraction

In any liquid-liquid extraction process, the exchange of materials between the two phases occurs by diffusion across the interface till the equilibrium is attained. To accelerate the establishment of the equilibrium, in the conventional extraction processes, the two phases are vigorously agitated. Equilibrium can also be attained without agitation but requires a much longer time. Since the time required is considered prohibitive, extractions are not made without accelerating the establishment of the equilibrium.

However, the conventional techniques cannot be used in the case of concentrated solutions and those containing insoluble residues. This difficulty can be avoided by making use of the new ' static extraction ' process, which does not require the mixing of the two phases by stirring [*Analyt. Chem.*, **39** (1967), 1903].

The extractions can be made by adding 10 ml. of the aqueous solution and about 2 ml. of the organic solvent in simple containers, like polyethylene bottles. The bottles are set aside overnight. Then the organic layer is removed and a fresh layer added. The bottles are set aside overnight again. The process is repeated until the desired extraction is attained. In case of dilute solutions, one overnight contacting gives complete extraction. Concentrated solutions require several contactings.

In the static extraction, the rate of diffusion is slowed down as the organic layer adjacent to the interface becomes saturated with the extracting species. The extraction rate is brought up to a practical level by the intermittent replacement of this layer with a fresh layer. As this organic layer builds up to saturation, only a small volume of it is necessary for each contacting. The method has been advantageously used for the determination of copper, gallium, tantalum and zirconium in plutonium, and is particularly useful whenever special problems exist.

Preparation of maleic thioanhydride

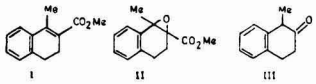
A method for preparing maleic thioanhydride has been reported for the first time [*Angew. Chem. int. Edit.*, **6** (1967), 874].

The method involves the preparation of a thio derivative by triturating 1,2,3,6-tetrahydrophthalic anhydride and $Na_2S_x.9H_2O$ in a mortar and then pouring into 10 per cent hydrochloric acid. The thioanhydride, thus prepared, is extracted with ether and isolated by vacuum distillation in 40-50 per cent yield with b.p. 81-83°C./0·1 mm. Thermal retrodiene fission of thioanhydride in an electrically heated quartz tube (2·5 × 30 cm.) at 430-50°C. with nitrogen as carrier gas (between 6·0 and 6·2 litres/hr) leads to maleic thioanhydride with about 50 per cent conversion and more than 90 per cent selectivity. The mixed product contains small amounts of decomposition products, mainly the thioanhydrides, which are separated by distillation. The thioanhydride boils at 72-74°C./10 mm.; it solidifies to pale yellow, translucent crystals (m.p. 28°C.) turning deep brownish yellow in air.

New synthesis of 1-methyl-2-tetralone

Highly substituted variants of 1-methyl-2 tetralone, a widely used early intermediate in the total syntheses of diterpenic and steroidal substances, can now be synthesized as a result of the development of a new synthetic procedure at the Department of Chemistry, Indiana University, Bloomington, Indiana [*Chemy Ind.*, (1967), 1252]. The new synthesis, unlike the earlier methods based on the utilization of preformed (hydro-) naphthalene ring systems, introduces the desired latitude for the construction of more complex β-tetralones.

The starting compound is acetoacetic ester which is C-alkylated with β-phenylethyl bromide and the product cyclized under the influence of sulphuric acid. Slight modification of the second reaction from the original Von Auwers procedure [*J. prakt. Chem.*, **109** (1925), 124] produces exclusively 1-methyl-3,4-dihydro-2-naphthoic acid in 74 per cent yield. [A mixture of keto-ester (1 g.) and concentrated sulphuric acid (5·5 g.) was maintained at −20°C. for 4 hr.] Esterification of the latter with methanol affords compound (I). Exposure of the olefinic ester to



I II III

m-chloroperbenzoic acid yields the epoxy-ester (II) which without purification is treated with aqueous acid. The consequent hydrolysis and decarboxylation of the glycidic ester lead to the desired compound (III).

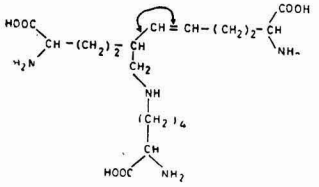
Glycoprotein-a, a new bovine milk protein

The isolation of a new protein, tentatively named glycoprotein-a, from bovine milk has been reported [*Biochemistry*, **6** (1967), 2388]. Glycoprotein-a differs from Υ-G-globulin and other previously characterized milk Υ-globulins in its carbohydrate content, amino acid composition, sedimentation coefficient, electrophoretic behaviour before and after reduction and alkylation, and serological behaviour. On gel electrophoresis, it shows a single band at *p*H 4·3 and several bands (4-5) at *p*H 9·1, thereby indicating that the observed polymorphism of the protein is probably genetically controlled. Based on the presence of a single methionine residue per molecule it is found to have a minimum molecular weight of the order of about 48000.

Milk from individual cows is fractionated and chromatographed according to Groves [*Biochem. biophys. Acta*, **100** (1965), 154]. Whey-F protein is then chromatographed on DEAE-cellulose with 0·005*M* phosphate buffer (*p*H 8·2) and the eluate (fraction 1F), thus obtained, is next chromatographed on phosphocellulose with 0·1*M* sodium phosphate at *p*H 6·0. The eluate (fraction $1F_2$) from the above moves as a single peak in the Perkin-Elmer electrophoresis apparatus; mobility $1{\cdot}26\times10^{-5}$ cm.²/V. sec. in 0·10 ionic strength veronal buffer (*p*H 8·5). But the presence of two components in the fraction is demonstrated by disc electrophoresis at acid *p*H and by ultracentrifugation at *p*H 7. The two components having sedimentation coefficients of 4*S* and 7*S* are finally separated by gel filtration on Sephadex G-200. The yield of glycoprotein-a is 50 mg. per litre of milk.

Merodesmosine, a new amino acid

The isolation of a new amino acid, $C_{18}H_{34}N_4O_6$, from borohydride reduced elastin from young ducklings (1-3 days old) has been reported [*Biochemistry*, **6** (1967), 2425]. Like desmosine and isodesmosine, the new compound incorporates the label from ^{14}C lysine in tissue culture experiments. From mass spectrum of the tetra-N-trifluoroacetyl tri-*n*-butyl ester (Mass 954), the compound appears to be derived from 3 molecules of lysine with the loss of two nitrogen atoms. On the basis of its empirical formula and relationship to lysine it has been named ' merodesmosine ' and assigned the structure



The presence of four nitrogen atoms as amino or imino groups and of six oxygen atoms as three carboxyl residues in the above structure has been chemically proved. However, since the position of the double bond has not been determined, the possibility of merodesmosine being as a mixture of geometric and structural isomers remains open.

A new chromatographic system for resolution of tRNA

A new reversed-phase chromatographic system capable of yielding superior resolution of transfer ribonucleic acids has been developed at the Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge. The most important feature of the new system is the use of a nonlinear concave gradient which (i) allows those tRNA species which are sensitive to small changes in NaCl concentration to elute under a gradually increasing concentration at the beginning of the chromatogram and (ii) at the end of the chromatogram, accelerates the entry into the mobile phase of those species less sensitive to changes in NaCl concentration and thereby maintaining resolution. In addition, the method is simple and samples may be directly assayed for amino acid acceptor ability. These advantages combined with the scale-up capability make the new system a valuable tool for both preparatory and analytical experiments.

A quaternary ammonium extractant, tricaprylyl-methylammonium chloride, in a Frean diluent, tetrachlorotetra-fluoropropane is supported as a thin film on hydrophobic diatomaceous earth. RNA dissolved in 2 ml. of the initial elution solution is sequentially eluted by NaCl gradient elution at flow rates of 0·5 or 2 ml./min. In addition to NaCl, the eluent contains 0·01*M* $MgCl_2$ and either 0·01*M* tris buffer at *p*H 7·0 or sodium acetate buffer at *p*H 4·5.

The column eluate is collected in approximately 10 ml. fractions and the absorbance at 260 mμ is measured with a Bechman DU spectrophotometer. The amino acid acceptance activity of selected fractions is directly determined as described earlier [*J. biol. Chem.*, **240** (1965), 3979]. The column is used repeatedly for up to eight runs. Any residual RNA is discharged between runs by passing approximately 500 ml. of a solution containing 0·5*M* NaCl plus 0·01*M* $MgCl_2$ and 0·01*M* buffer through the column. As a precaution, columns are stored at 4°C. between experiments to minimize extraneous bacterial growth [*Biochemistry*, **6** (1967), 2507].

Astrophysics and Space Science

This new journal in the field of cosmic physics has been recently started by D. Reidel Publishing Co., Dordrecht, Holland. Two volumes of four issues each would be published in a year.

The journal publishes original papers on astrophysics, in English, French, German and Russian. Papers in languages other than English are provided with an English abstract. The journal covers the entire domain of astrophysics and allied fields of cosmochemistry, dynamics, etc., with emphasis on topics opened up by space research. It also contains

observational and theoretical papers as well as papers concerned with instrumentation.

The subscription for one volume of 4 issues is $ 25.00 for institutions and $ 8.50 for individuals.

Central Electrochemical Research Institute, Karaikudi

Among the important achievements of the Institute recorded in its annual report for 1966 are the development of alkaline manganese dioxide wet cells (capacity 500 amp. hr) from indigenous manganese dioxide ores; fabrication of tantalum capacitors, development of a jelly to remove deteriorated paints; and the modification of the Johnston-Ubbelohde theory of the wedge effect to take into account the high rate of movement at the mercury/glass interfaces. The seventh seminar on electrochemistry was held during the year.

The fluidized bed technique, with a bed of inert materials, has been made use of for both electroplating and electropolishing of copper. During the electroplating of copper on steel, fluidization avoids tree formation and gives uniform plating of corners. Suitable baths have been developed for electrodeless copper plating of mild steel, direct platinum plating of titanium and cadmium plating. The new baths give smooth and adherent deposits.

Of the different electrochemical oxidation-reduction reactions studied during the year with stationary and/or rotating electrodes, mention may be made of the reductions of pictrite, *m*-nitrobenzene sulphonic acid and citrol.

Air-depolarized carbon electrodes have been developed from by-product carbon blacks obtained from the combustion of naphtha. A new type of self-regenerating alkaline manganese dioxide system with improved performance characteristics has been developed for use in the alkaline manganese dioxide cells.

Industrial wastes like tannic acid, coffee residue, rice husk, etc., have been tested as inhibitors for the corrosion of mild steel, copper, zinc and aluminium in hydrochloric acid and found to give favourable results. Molasses, groundnut-shell extract and gall nuts have been found to be good inhibitors for the corrosion of ferrous and common non-ferrous metals in sulphuric and hydrochloric acids.

The developmental work on anodic phosphating has resulted in the simplification of operating conditions and reduction in the cost. The phosphate coating produced by the anodic process is also superior to that produced by the chemical process in respect of corrosion resistance, maintenance of paint gloss and uptake of satin finish.

The anodic behaviour of silver in hydrochloric acid has been explained in terms of solid state and a mechanism based on *p-n* junctions proposed to account for the oscillations of anode potential with time under constant current conditions. A fixed area mercury electrode, with sensitivities greater than the conventional dropping mercury electrode, has been developed and found to be suitable for determining concentrations of the order of $10^{-4}M$/litre.

A new method has been developed for the deposition of thin layers of silver sulphide at room temperatures. These thin films, when given gold contacts by vacuum deposition, are found to have satisfactory photoconductive response.

Regional Research Laboratory, Hyderabad

The latest annual report (1966-67) of the laboratory presents in detail its research activities during the year. The processing of cottonseed (20 tonnes/day) has been streamlined and a solvent extraction plant to produce 5-6 tonnes of high protein cottonseed flour has been commissioned. The laboratory has prepared detailed project reports for the setting up of low temperature carbonization plants for the Singareni Collieries Co. Ltd, and the Government of Maharashtra.

An aluminium-zinc oxide primer has been developed with a view to replacing the imported red lead primer. This primer has been found successful on large-scale trials by the railways, defence and the chemical industry. An anti-corrosive ship-bottom paint has been developed and found to be successful after prolonged raft tests. Besides, several other surface-coating compositions have been developed. Phospholipids, free of neutral lipids, have been isolated from *Hydnocarpus wightiana*.

The laboratory has continued to manufacture pyrometric cones for the industry. The process for the production of PCE cones, developed at RRL, has been released to the industry. Microwave ferrites, produced for defence, have proved successful in field trials.

Several β-phenylethylamine derivatives, having chlorine in 2,3-, 2,4-, 2,5- and 3,4-positions, have been prepared. A few members have shown potent cardiovascular and hypotensive action. Studies on the manufacture of cyclohexane by benzene hydrogenation have been completed and work is in progress on the reduction of aniline to cyclohexylamine. Lyophilized snake venom, papain and a few other biochemicals have been manufactured for export. A feasibility report on the production of terpineol and a project report on the manufacture of benzyl cyanide have been submitted to commercial entrepreneurs.

Six processes evolved by the laboratory have been released to the industry. These are for benzyl chloride, pyrometric cones, light kaolin BP, cardanol, citicide (a new pesticide) and barium-potassium chromate pigment.

National Botanic Gardens, Lucknow

The annual report of the gardens for the year 1966 besides surveying the progress of research in various divisions gives an idea of the main future research programmes. A programme for the evolution of improved and disease-free varieties of economic plants has been taken up, and experimental cultivation of aromatic and medicinal plants on saline and alkaline soils is under way. A plan has been drawn for establishing a botanical garden for growing salt-tolerant species at Banthra.

A large number of ornamental and cultivated trees, shrubs, creepers and annuals of Indian gardens were examined critically from the point of view of their identification and standardization of nomenclature. Among the major research

projects in hand are: morphological and taxonomical studies of Indian angiosperms and pteridophytes; animal food production from sewage; cultivation of edible mushrooms; and preparation of horse dung compost and synthetic compost. Pharmacognostic studies on the following Indian medicinal plants used in the indigenous systems of medicine have been undertaken: *Eclipta prostrata* Roxb., *Wedelia calendulacea* Less., *Swet punarnava, Abrus precatorius* L., *Alpinia speciosa* Schum., *A. calcarata* Roxb., *Cassia* spp., *Casearia tomentosa* Roxb., *Alangium salvifolium* L., *Barringtonia acutangula* Gaertn, *Abutilon hirtum* G. Dan. Resins obtained from *Pistacea lentiscus* and *Boswellia carterii* have been found to be satisfactory substitutes for the imported Canada balsam, in the preparation of microscopic slides.

Several species of medicinal and aromate plants have been experimentally cultivated and chemically analysed. Plants of *Mentha arvensis* giving oil with menthol content as high as 68·6 per cent have been grown. A compound identified as eroidictyol has been isolated from the roots of *Garcinia livingstonei* T. Anders. Euphorbol, a tetracyclic triterpene having the formula $C_{30}M_{50}O$, has been isolated from the methanolic extracts of the whole plant of *Euphorbia dracunculoides* Lam. Besides paridin and paristyphin, reported earlier, monoglucoside of diosgenin ($C_{33}H_{52}O$) has been isolated from *Paris polyphylla* Smith, in 0·5 per cent yield. The pericarp of *Anacardium giganteum* has yielded a new acid, $C_{18}M_{28}O_2$, m.p. 81°C., whose structure has been established as 3-undecylsalicylic acid. Two triterpenoid compounds, melting at 231° and 245°C. respectively, were isolated in pure form from *Physalis franchetii* through absorption chromatography. A new disaccharide, m.p. 161°, was isolated from *Albizzia procera* seed gum.

Cytogenetic and breeding studies on several economic plants, viz. Amaranthus, Canna, Gloriosa, Verbena, Antirrhinum, Petunia, Ruellia and Zephyranthes, have been undertaken. Improvements in some horticultural plants, viz. Rose, Chrysanthemum, Portulaca, Acidanthera, fruiting plant like grape, papaya and Cape gooseberry, and essential oil bearing plants like Mentha and *Rosa damascena* by radiation-induced mutation have been introduced.

Other projects studied during the year are: (i) study of genetics of fragrance; (ii) exploitation of hybrid vigour; (iii) breeding grapes for earliness; (iv) breeding sunflower for high oil content and its adaptability to alkaline soil; (v) raising large flowered chrysanthemum varieties; (vi) improving quality of grapes; (vii) tissue and organ culture of medicinal and other economic plants; (viii) production of virus-free sweet potatoes; and (ix) investigation on lipid bearing seeds and fruits for utilizing the fats and the active principles.

Prof. S. J. Arceivala

Prof. S. J. Arceivala has been appointed Director, Central Public Health Engineering Research Institute, Nagpur.

Prof. Arceivala (b. January 17, 1926) took his B.E. (Civil) from the Bombay University (1947) and M.S. (Engng) from the Harvard University (1955).

He has been actively engaged in teaching and research in public health engineering and as a consultant for about 20 years. Prior to his appointment as Director, CPHERI, Prof. Arceivala was working as Vice-Principal and Head of Civil and Sanitary Engineering Department in the V.J.T. Institute, Bombay, where he was responsible for developing post-graduate courses in public health engineering. He was invited by the World Health Organization in 1966 to prepare a working paper on Public Health Engineering (PHE) Education and to attend the meeting of the WHO Expert Committee on PHE Education at Geneva in July 1967. He was also invited by the WHO to act as a temporary Adviser during the Inter-Regional Seminar on 'Water Pollution Control' held in November 1967 in New Delhi.

Prof. Arceivala has been a consultant to a number of municipalities and private industries on the treatment of water, sewage and industrial wastes. As a consultant to the Bombay Mill-owners' Association, he was responsible for developing techniques for re-use of waste water, which have now been implemented by most of the textile units in Bombay. Prof. Arceivala was appointed as a consultant to the Bombay Municipal Corporation to survey the water requirements of 45 different industries in Bombay and devise ways and means of conserving and re-using water in chemical, pharmaceutical, textile and other industries.

Prof. Arceivala introduced, for the first time, cathodic protection in sewage treatment plants. He has also been responsible for the first 'item-rate' tender for municipal sewage treatment plants; design of electroplating and chemical waste treatment facilities; extended aeration plants; plumbing and fire-fighting arrangements for skyscrapers; upflow-type filter for industrial water re-use plants; and framing bye-laws for discharge of industrial wastes to sewers.

Prof. Arceivala has been a member of the Executive Council of CPHERI, the Scientific Subcommittee of the Executive Council Advisory Committee of the CPHERI Zonal Centre, Bombay, and the Editorial Board of the Institute's quarterly journal, *Environmental Health.* He has published 25 papers

Prof. Arceivala is a member of the American Society of Civil Engineers, American Water Works Association, Institution of Engineers (India), and several other national and international societies. He is also a member of Sectional Committee for PHE Plants and Equipment of the Indian Standards Institution and a member of the Faculty of Technology and Board of Studies of the Universities of Bombay and Baroda.

Announcements

▪ *The Twelfth Conference on Analytical Chemistry in Nuclear Technology* will be held in Gatlinburg, Tennessee, USA, during 8-10 October 1968. The theme of the conference is "The role of the analytical chemist in research on the production and chemical properties of the actinide elements and in the elucidation and solution of problems in the field of environmental pollution and related areas".

Simultaneously with the conference, an exhibition of modern analytical instruments and laboratory equipment would be held. For this, facilities would be available to manufacturers and dealers in laboratory supplies to exhibit their products. Further information regarding the conference and the exhibition may be obtained from Mr L. J. Brady, Chairman, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37930, USA.

▪ *International Courses in Hydraulic and Sanitary Engineering*— The Delft Technological University in cooperation with the Netherlands Universities Foundation for International Cooperation would be conducting these courses at Delft during 17 October 1968 to 6 September 1969.

The course on hydraulic engineering would comprise tidal and coastal engineering; reclamation; rivers and navigation; theoretical and experimental hydraulics; and hydraulic structures. The course in sanitary engineering, divided into two parts, would include (i) control of water pollution and the provision of drinking and industrial water in densely populated industrialized areas and (ii) problems dealing with drinking water supply, sanitation and health administration in the agricultural and initial phases of development.

Further details regarding the courses may be obtained from the Registrar, Netherlands Universities Foundation for International Cooperation, 27 Molenstraat, The Hague.

▪ *An International Conference on Shear, Torsion and Bond in Reinforced and Prestressed Concrete*, sponsored jointly by the P.S.G. College of Technology, Coimbatore, and the Structural Engineering Research Centre, Roorkee, will be held in the former's premises during 14-17 January 1969. Papers with direct bearing on the theme of the conference would be presented. Further particulars can be obtained from Dr V. Ramakrishnan, Professor and Head, Department of Civil Engineering, P.S.G. College of Technology, Coimbatore 4.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES, 1968

Date	*Conference*	*Place*
19-23 Aug.	Third International Peat Congress	Quebec
20-25 Aug.	Seventh World Power Conference	Moscow
21-28 Aug.	Sixth International Congress on Acoustics	Tokyo
25-30 Aug.	Sixth International Symposium on the Reactivity of Solids	Schenectady, NY
25-31 Aug.	Twenty-fourth International Congress on Physiological Sciences	Washington, DC
25-31 Aug.	Twelfth International Congress on the History of Science	Paris
25-31 Aug.	Twelfth International Congress on Cell Biology	Brussels
25-31 Aug.	Twelfth International Congress on Applied Mechanics	Stanford, USA
26-31 Aug.	Fifth International Photobiology Congress	Dartmouth, USA
26-31 Aug.	International Conference on Cloud Physics	Toronto
28 Aug.-5 Sept.	International Conference on High Energy Physics	Vienna
1-6 Sept.	Twelfth International Congress on Haematology	New York
2-6 Sept.	International Fermentation Symposium	New Burnswick, USA
2-7 Sept.	International Conference on Coordination Chemistry	Haifa and Jerusalem
9-13 Sept.	Fifth International Congress on Surface Activity	Barcelona
9-14 Sept.	Fourth International Exhibition and Congress of Laboratory Measurement and Automation Techniques in Chemistry	Basel, Switzerland
18-20 Sept.	International Surface Mining Congress	Minneapolis
20-24 Sept.	Second International Congress on Marine Corrosion and Fouling	Athens
24-26 Sept.	International Power Sources Symposium	Brighton
Sept.	International Congress on Essential Oils	Tiflis
Sept.	Third International Wheat Genetics Symposium	Adelaide
Sept.	Conference of the International Federation for Documentation	Moscow
Sept.	International Congress of the Pharmaceutical Sciences	Hamburg
Sept.	Fourth International Conference on Water Pollution Research	Prague
Sept.	Fifth International Symposium on Chromatography and Electrophoresis	Brussels

▪ *The Second International Symposium on Acoustical Holography*, sponsored by the Douglas Advanced Research Laboratories, would be held during 6 and 7 March 1969. Further particulars can be obtained from the Secretary, Second International Symposium on Acoustical Holography, Douglas Advanced Research Laboratories, McDonnell Douglas Corporation, 5251 Bolsa Avenue, Huntington Beach, California 92647, USA.

▪ *Raja Ravi Sher Singh of Kalsia Memorial Cancer Research Award*— Nominations from Indian nationals are invited for this Rs 900 award for (i) outstanding research work in the experimental or clinical aspects of cancer carried out during 1967 or (ii) outstanding work in the organization and conduct of any service or service-cum-research programme in the field of cancer prevention and treatment during 1967. Details of the work carried out together with a short biographical sketch and reprints of papers published may be sent to the Director-General, Indian Council of Medical Research, Post Box 494, New Delhi, before 31 August 1968.

▪ *The Indian Society for the Study of Reproduction* would now be known as the Indian Society for the Study of Reproduction and Endocrinology. Applications for membership of the society giving name, qualifications, occupation, address, field of interest, publications and membership desired (ordinary or life) should be sent to the Honorary Secretary, the Indian Society for the Study of Reproduction and Endocrinology, Reproductive Physiology Unit, Seth G.S. Medical College, Parel, Bombay 12. The fee is Rs 10.00 for ordinary membership and Rs 250.00 for life membership.

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