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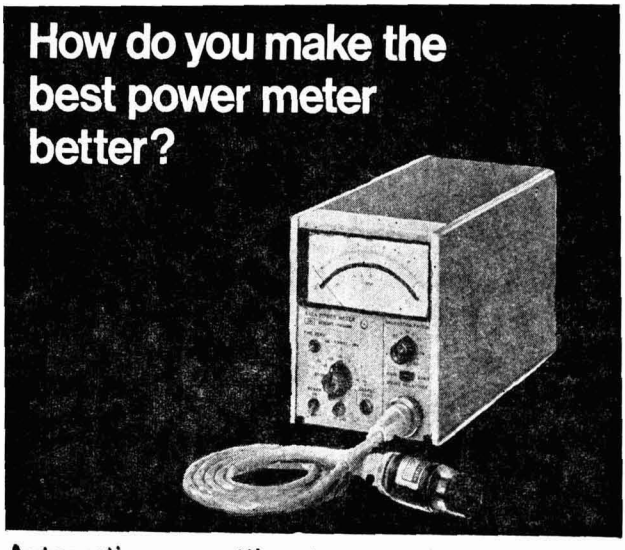

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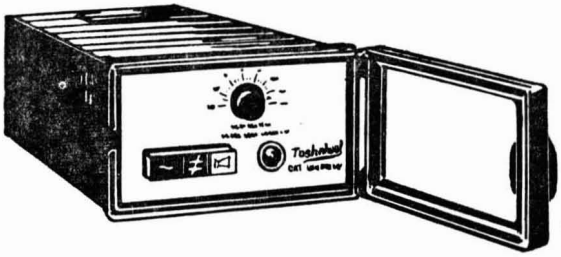

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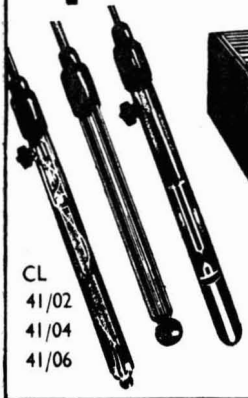

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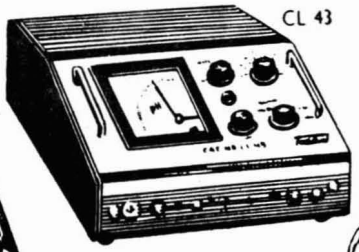

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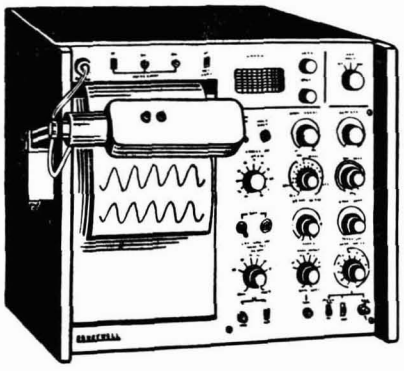

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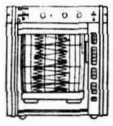

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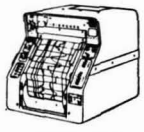

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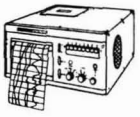

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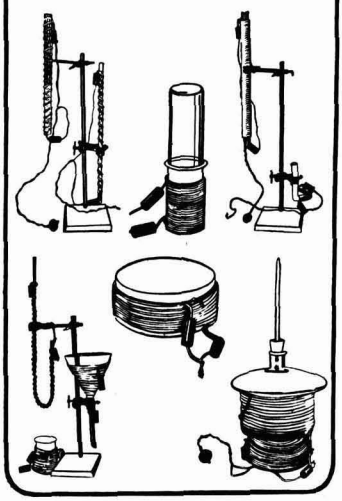

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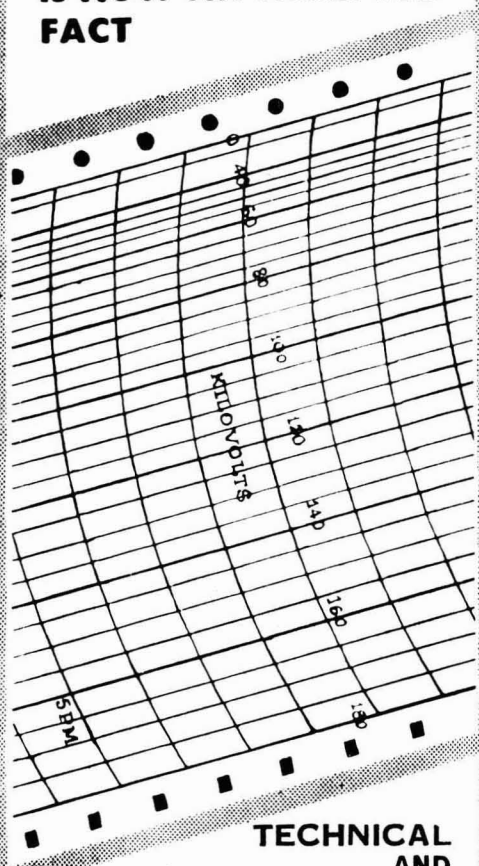

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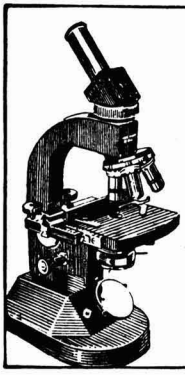

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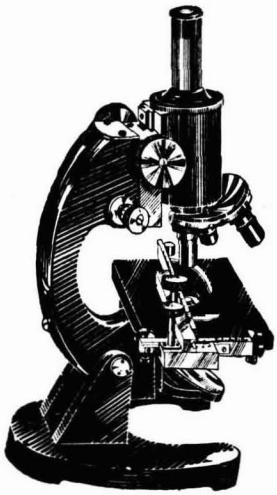

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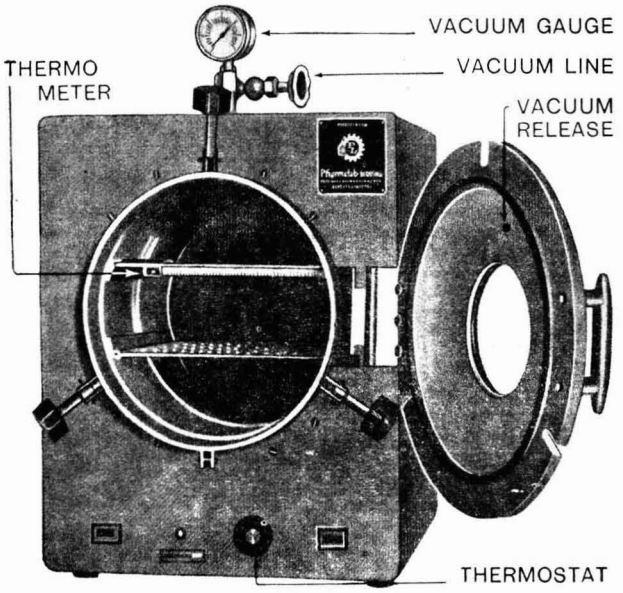

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Current Topics

How to Cope with Accelerating Growth of Scientific Information: US Committee's Report

LARGE investment on research and development activities has, in recent years, become a prominent feature of the national spending pattern in most of the countries, particularly in the advanced ones. USA is currently spending to the tune of $ 27 billion per year on these activities. An inevitable consequence of this trend has been the growth of scientific and technical information in geometrical progression. During the major part of this century, published research information has been doubling every 10-15 years. Roughly 2 million original research papers in all fields of science and technology are currently published every year in some 30,000 specialized journals. And the problem of dissemination of scientific and technical information, the main product of research effort, is assuming greater and greater importance and has been engaging the attention of various national and international agencies. The recent report* of a 25-member Committee of Scientific and Technical Communication (SATCOM) set up jointly by the National Academy of Sciences and the National Academy of Engineering, USA, provides some guidelines as to how the problem can be tackled.

Calling for steps to avert under-utilization of the available scientific and technical knowledge, the Committee emphasizes the need for maintaining the pluralistic, diverse nature of communication activities in science and engineering — as opposed to the creation of any monolithic, centralized system. The pattern advocated for the vigorous growth of scientific and technical communication system is " to be pluralistic, user-oriented, rapidly evolving under strong federal support — but with strong self-coordination to match the growing responsibilities of the private organizations ".

Commenting on the status of the existing information dissemination systems, the Committee feels that there is no evidence of critically inefficient operation or catastrophic failure of these systems, their basic structure being sound. However, the problems posed by expanding needs of users make it necessary to take measures directed towards more effective coordination, planning and management.

Notable among the 55 recommendations made by the Committee is one pertaining to the establishment of a Joint Commission on Scientific and Technical Communication for stimulating greater coordination among private groups and bringing them into close touch with government agencies. The Academies, with their established prestige, non-governmental status, and close working ties with scientists, private organizations, and federal agencies, are considered to be the best possible base for the Commission.

Another recommendation of the Committee outlines a philosophy of shared responsibility among government and private organizations for the effective communication of scientific and technical information, so that through the cooperation of those who support research and development work, the information becomes truly available. This should go beyond ' mere publication of isolated tidbits scattered through a multitude of journals ' towards acceptance of a broader responsibility to recognize the preparation and dissemination of information as an integral part of the research work.

The report draws pointed attention to the crucial role which learned societies can play in the dissemination of information. The responsibilities expected of the societies are " improving the quality, timeliness and techniques of producing and distributing primary literature; assuring adequate basic abstracting and indexing of the primary information; stimulating the reprocessing and repackaging of information for special user groups; and conducting ' exploratory and innovative studies ' using qualified scientists, engineers and practitioners to evaluate the performance of their information services ". A still more important function which societies can take upon themselves is to encourage the preparation of critical review articles and data compilations, an effort which requires great intellectual creativity. There is also great need for such activities, which organize and evaluate what is known about a subject and present it in a language that can be understood. In the opinion of the Committee, the for-profit information handling organizations have a critical role to play in providing specialized information services to small groups (down to 1000 persons) and their capabilities should be used to the fullest.

Dissemination of scientific information, like all other scientific activities, is an international problem and the responsibility of all nations of the world. The problems identified and the recommendations made by SATCOM have universal applicability and should interest all those concerned with the generation and dissemination of scientific information. The report provides valuable guidelines for the formulation and moulding of policies and practices in respect of communication of scientific information, so that the expanding needs of the users are effectively and efficiently met.

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Seminar on Crystallography*

R. SRINIVASAN
Centre of Advanced Study in Physics, University of Madras, Madras

THE Centre of Advanced Study in Biophysics and Crystallography, University of Madras, conducted its fifth annual seminar lasting for three days (5-7 February 1969). Due to unavoidable circumstances, it could not be held at the premises of the new building of the Centre and the venue was shifted to the Physics Department of the Indian Institute of Technology, Madras. There were 82 contributors and participants and the number of papers presented was 46, representing about 20 institutions all over India. The large number of papers compared to the previous seminars is indicative of the growing strength of crystallography and structural research in India.

There were in all four sessions which can be broadly classified into (1) Neutron studies, (2) Structural crystallography, (3) Theoretical methods, and (4) General crystallography.

In the first group, there was an interesting paper by Dr S. K. Sikka (Bhabha Atomic Research Centre, Bombay) on the use of anomalous scattering in neutron diffraction for the determination of the structure of $Sm(BrO_3)_3.9H_2O$. This is the first application of the method to a practical example, although recently the theoretical possibilities have been discussed in the literature. A paper by S. N. Momin, A. Sequeira and R. Chidambaram (Bhabha Atomic Research Centre, Bombay), presented by Dr R. Chidambaram, described a fully automatic neutron diffractometer fabricated at Trombay. It is heartening that such a diffractometer has been completely built in India from available components. Two other papers dealt with neutron diffraction study, one on the crystal structure of potassium oxalate monohydrate, and the other on the structure of sodium thiosulphate pentahydrate.

In structural crystallography, a number of structure determinations by X-ray methods were reported. Notable among these are studies on (a) organic compounds, (b) inorganic compounds, (c) organometallic complexes, and (d) compounds of biological interest.

Dr L. M. Pant (National Chemical Laboratory, Poona) presented the crystal structural features of some substituted benzene compounds. The crystal structures of sparteine N_{16} oxide sesquiperchlorate and xanthone were presented by Dr S. N. Srivastava (University of Allahabad) and by S. C. Biswas (Calcutta) respectively. Dr K. V. Muralidaran (Bhabha Atomic Research Centre, Bombay) presented the crystal structure determination of 2-imino-4-thiozolidinone-5-acetic acid. The molecular configuration of ishwarone, which could not be established by chemists by normal methods, was discussed by G. Srinivasamurthy (Indian Institute of Technology, Madras); the correct structure arrived at by X-ray methods was presented. The papers by T. Srikrishnan and Mrs Vasantha Pattabhi (University of Madras) dealt respectively with the crystal structure and molecular conformations of 1-amino cyclooctane carboxylic acid hydrobromide and of D-phenylalanyl L-phenylalanine-O-methoxy hydrobromide.

Dr G. B. Mitra (Indian Institute of Technology, Kharagpur) presented the crystal structure determination of biguanide acid sulphate monohydrate. He has used a modified form of the direct method for structure determination. J. K. Mohana Rao (Indian Institute of Science, Bangalore) presented the structure of ferroelectric glycine silver nitrate and Dr N. R. Kunchur (Poona University), the crystal structure of palladium *n*-propyl mercaptide. An accurate analysis of the crystal and molecular structures of ornithine was presented by S. Guha (Saha Institute of Nuclear Physics, Calcutta). This had an interesting feature, namely that the structure as a whole was non-centrosymmetric crystallizing in the space group $P2_1$, although the asymmetric unit had a centrosymmetric configuration about the copper atom.

The crystal structure of $Ca_2Sr(CH_3CH_2COO)_6$ was presented by Dr M. Chalam (University of Madras). The structure shows disorder, manifesting a probable rotation of two of the six methyl groups; its possible relation to ferroelectricity was pointed out.

Among the inorganic structures, the following were reported: Structure and chemical composition of vauxite, by Dr B. Rama Rao (Regional Research Laboratory, Hyderabad); Structure of sodium 2-oxo-heptylate, by S. C. Jain (Indian Institute of Technology, Bombay). Studies on calcite type compounds by K. Satyanarayana Murthy (Osmania University, Hyderabad), on single crystal transformation of orthorhombic Sb_2O_3 to orthorhombic Sb_2O_4 by P. S. Gopalakrishnan (Indian Institute of Science, Bangalore), and on potassium mercuric tribromide monohydrate by V. S. Yadav (Bhabha Atomic Research Centre, Bombay) were presented.

In crystallographic methods, a paper was presented by K. K. Chacko (University of Madras) on the Fourier treatment of anomalous dispersion components from X-ray diffraction data. This followed the earlier paper by R. Srinivasan and K. K. Chacko (University of Madras) and reported further tests of the theory and extension to the centrosymmetric case. The need to take into account anomalous dispersion correction in centrosymmetric crystals was stressed in a paper by M. N. Sabesan (University of Madras) with illustration of how the electron distribution gets affected without these corrections. Dr S. Parthasarathy (University of Madras) presented a paper on tests for semi-isomorphism, using higher moments of

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intensities. This type of semi-isomorphism is met with in protein crystallography, namely two different derivatives from the same parent compound may differ in the positions of the heavy atom substitution. In a paper on beta synthesis and its application to crystal structure analysis presented by Dr S. Parthasarathy it was shown that in the crystal, if the known part contribution is large, some of the input atoms, which are wrong in their positions, will come out as negative peaks in the beta synthesis, unlike in the ordinary heavy atom synthesis. The former can thus claim a superiority over the heavy atom synthesis.

The session on general crystallography opened with a paper by Prof. S. Chandrasekhar (University of Mysore) on the optical properties of liquid crystals. Some of the intriguing optical properties of liquid crystals were neatly explained on the basis of theoretical models making use of the Jones calculus for optical systems and the dynamical theory of dispersion. Considerable interest in the structure of sodium chlorate and sodium bromate has been evinced recently, since the two structures showing the same sense of optical rotation have been shown to have opposite absolute configurations. Studies on mixed crystals of these two are of interest and a paper was presented by Dr K. S. Chandrasekharan (Madurai University). There was also a paper from his group on interferometric methods using diffracted beams. Dr S. Bhattacherjee (Indian Institute of Technology, Kharagpur) presented a paper on the theory of low angle scattering by clusters of curved crystallites. There was a paper by S. V. Suryanarayana (Osmania University, Hyderabad) on thermal expansion in relation to the structure of some scheelite-type crystals. There were a few papers dealing with crystal growth and stacking faults in close-packed crystals and related topics. Krishan Lal and S. K. Peneva (National Physical Laboratory, New Delhi) presented a paper on the study of shapes of diffracting planes by X-ray Laue technique, while another paper by Prof. A. R. Verma and S. K. Peneva (National Physical Laboratory, New Delhi) dealt with X-ray investigations on the growth of Cd whiskers. The following three papers were presented by the group from Banaras: (1) X-ray diffraction from hexagonal close-packed crystals with deformation stacking faults: Effect of solute segregation at faults in alloys; (2) X-ray diffraction from double hexagonal close-packed crystals with deformation stacking faults; and (3) Stacking faults in double hexagonal close-packed crystals. Dr Talapatra (Indian Association for the Cultivation of Science, Calcutta) presented the determination of elastic constants of anthraquinone from diffuse X-ray reflections and the evaluation of its Debye temperature by an extension of Houston's method.

Prof. G. N. Ramachandran (University of Madras) presented an interesting new possibility of stabilization of the structure of collagen via water molecules in the structure. There were three other papers reporting the analysis of the available crystal structure data with regard to conformation and other details. One was about the conformation about the P-O and C-O bonds in crystal structures of phosphoesters by A. V. Lakshminarayanan and V. Sasisekharan (University of Madras). The second was on the analysis of the crystal structures of carboxylic acid presented by P. K. Ponnuswamy (University of Madras) and the third on the structural features of lactones by V. Kalyani (Indian Institute of Science, Bangalore). An important structural feature of the lactone group was reported, namely that the group is planar and the nominally equivalent C-O distances about the ring oxygen atom are asymmetric and so on. There was a paper on the crystal orientation in natural cellulose fibres by Dr N. E. Dweltz (Ahmedabad Textile Industry's Research Association, Ahmedabad).

A Study of the Oscillations of a Viscous Fluid Drop Relatively at Rest in Another Viscous Fluid Medium

S. V. SUBRAMANYAM & E. S. R. GOPAL

Department of Physics, Indian Institute of Science, Bangalore 12

THE dynamics of liquid drops or gaseous bubbles moving in various media is important in many physico-chemical and engineering processes. In the practical applications, one deals with a collection of particles moving together. If the assembly is dilute (a few drops in a large volume), the interaction between the various drop fields can be neglected and the theoretical problem reduces to that of a single drop moving in another medium. If the assembly is concentrated, statistical methods have to be applied. In view of the many applications, the subject has been studied by a large number of workers both experimentally and theoretically.

In an analysis of the motion of a single drop in a fluid medium, the various properties of the two phases like the densities (ρ, $\hat{\rho}$), the kinematic viscosities (ν, $\hat{\nu}$), the interfacial tension T and external conditions of pressure, acceleration, etc., affect the experimentally observed quantities like the terminal velocity U, drag C_D, shape, oscillations, breakup, and so on. All these observed data are interdependent (e.g. the drag or the oscillation frequency depends upon the shape) and an analysis of any one will not be complete without due weightage to the others. The present paper presents the results of a detailed study on the oscillations of a drop of fluid in an outside fluid medium. Factors such as the shape of the drop, the velocity fields present, the magnitude of the perturbation of the interface and the various fluid properties are taken into account.

Most of the earlier calculations presented by different workers are applicable in only certain limiting cases like inviscid flow, or flow in free space, or flow around a spherical drop, and so on. But experimental results show that, in practice, rather large deviations from the limiting cases arise, probably because of the interaction among the inertial, pressure, viscous and interfacial terms. Hence, it was found desirable to carry out detailed calculations on the oscillations of drops and bubbles incorporating all the terms arising from the viscous effects, the deformation of the drop, the presence of two media with different properties and inertial motion of the drop with terminal velocity.

The present communication first gives a brief outline of the drop dynamics, with special reference to the oscillations and the various factors which influence the oscillations. The oscillations of a spherical liquid drop at rest in a fluid medium are next discussed. Finally, the oscillations of a stationary liquid drop of deformed shape are treated.

Factors Affecting Drop Oscillations

Boundary Conditions

The general features of the dynamics of a liquid drop have been reviewed by Lane and Green[1], Kintner[2], Hsieh[3] and many other workers. Basically, the motion of a liquid drop differs from the motion of a solid sphere in that it is a two-phase problem with a deformable interface and that there are velocity fields both inside and outside the drop. Hence, in such a problem the boundary conditions are to be applied carefully[4]. These conditions are that the normal and tangential velocities should be continuous and so also the stresses. In the condition for the normal stress, the contribution from the interfacial tension has to be included.

Types of Oscillations

Basically, the oscillations can be classified into three types[2,5,6]: (i) prolate-oblate oscillations about an equilibrium spheroidal shape, (ii) oscillations about axes 90° apart in the horizontal plane, and (iii) eccentric rotation about the vertical axis, while the horizontal axes remain constant. Oscillations of type (i) correspond to the familiar Lamb's oscillation modes for the lowest symmetric mode. But there are other modes as well and Lamb's general expression for the frequency of oscillation (σ in rad/sec) is

$$\sigma^2 = \frac{l(l-1)(l+1)(l+2)T}{[(l+1)\hat{\rho}+l\rho]a^3}$$

where $\hat{\rho}$ is the density of the internal phase; ρ, the density of the external phase; and a, the radius; the mode of frequency l is related to the perturbed drop surface $r = 1+\epsilon_0 \times P_l (\cos\theta) e^{i\sigma t}$. The lowest asymmetric mode ($l = 1$) is a pure centre of mass shift of the drop; its restoring force against displacements and its frequencies are consequently zero. The lowest symmetric mode ($l = 2$) represents the prolate-oblate oscillations. It takes minimum of energies and is the most common mode observed in experiments. The lowest nonzero asymmetric mode ($l = 3$) is a mass asymmetric oscillation of the drop. The higher modes can similarly be described, but they are usually not met with. The various modes and the oscillation parameters are given in Fig. 1. Many of these frequency modes from $l = 2$ to $l = 8$ have been observed by Schoessaw and Boumeister[7]. They studied the frequencies by resting the drop over a hot plate in its own superheated vapour atmosphere. They found that generally the observed frequencies are less than those predicted by Lamb for the various modes by about 10%. The large amplitude of oscillation was considered to cause greater inertia and hence smaller frequency. We

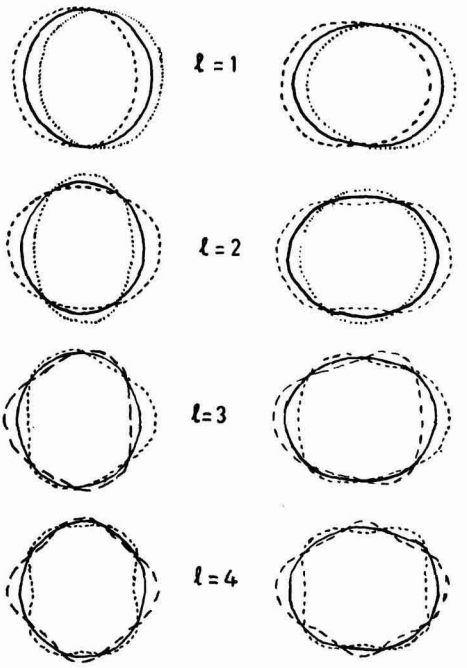

Fig. 1 — Modes of oscillation of a drop [$l = 1, 2, 3, 4$; $r = 1+\epsilon_1 P_2(\xi)+\epsilon P_l(\xi)$ refers to the deviation of the drop from the spherical shape]

have tried to account for this quantitatively by considering the oscillations of a deformed drop and find that the frequencies can indeed be lowered by ~10%. Similar discrepancies have been observed in a large number of cases. For instance, Constan and Calvert[6] studied the dependence of the frequency of oscillation on various factors like the drop diameter, the backstream velocity and the amplitude of oscillation. Again the frequencies were lower than those predicted from Lamb's equation by 20-40%. The oscillation of free drops in almost all cases will be of type (i), whereas in cases such as supported drops and some large liquid drops with low viscosity and surface tension, types (ii) and (iii) occur[5,6,8]. For a rotating liquid drop toroidal and transverse shear modes of oscillation have been studied by Chandrasekhar[9], Rosenkilde[10] and Rossner[11], whereas the ordinary oscillations for a compressible fluid sphere have been treated briefly by Champetier and Larger[12].

Causes of Oscillations

Except in the cases where the oscillations start due to an external oscillating pressure field or an initial disturbance of the interface, the reasons for the natural occurrence of oscillations during the motion of a drop are, as yet, obscure. Many causes are proposed, like vortex shedding and turbulence in the wake, mass and heat transfers, turbulence in the velocity fields, interaction between the surface energy and the hydrodynamic energies, and so on. It is worth while to investigate in detail the validity of these causes as they will decide the applicability of the theoretical results in the light of the experimental observations.

Vortex shedding and wake turbulence — Though these two causes can be treated independently of each other, the close interrelation between the two gives a valid cause for oscillations to start in most of the cases. Their importance to the initiation of oscillations has been recognized by many workers[13-20]. It has been observed in many cases that oscillations start in falling drops with a certain minimum Reynolds' number and Weber number. Winnikow and Chao[13] obtained the minimum values of Re and We to be of the order of 800 and 4·0 respectively, whereas Hartunian and Sears[21] as well as Saffman[22] suggested $We_{\min} = 1{\cdot}59$ for gas-liquid systems. A comparison between the dependence of the drag coefficient and the shape oscillation parameters on the Reynolds' number reveals some striking similarities. At low Re, when the drop remains in a spherical shape, the drag decreases with Re just as for a solid sphere. For $Re \gtrsim 80$, when the drop shape departs from the spherical shape, the drag tends towards a minimum. For higher Re ($\gtrsim$800), the drag increases with Re and in this region, the oscillations set in spontaneously. In this regime[18,19,23], the turbulence in the wake becomes quite pronounced. The periodic detachment of a double row of vortices which sets in when Re is a few hundred becomes quite asymmetric and a randomly oscillating pressure field will be impressed on the drop surface. The mechanism of the detachment of these vortices in the rear of the drop is still not clear. However, in many cases a plot of Strouhal number (fd/U) against Re reveals certain interesting features. At low Reynolds' number the variation is linear (i.e. the frequency of eddies $\propto U^2$), which is as should be expected. But soon the Strouhal number reaches a maximum at Re~1000 and thereafter remains almost constant or tends to decrease[24]. The former variation at low Re, which is quite common, has been verified by Magarvey and Bishop[18] and Elzinga and Banchero[16], whereas the latter is difficult to explain. Gerrard[17] has quite recently analysed the situation by considering the growth and detachment of a vortex from a body as due to (i) intense circulation in the shear layer which strengthens it, and (ii) the approach of an oppositely signed vortex which tends to detach it from the drop. This is the basic mechanism which determines the vortex shedding frequency. Several empirical relations exist connecting the frequency of vortex detachment and the Reynolds' number; for example, that of Rayleigh[25] for the flow past a circular cylinder. But no precise mathematical computations have been done to relate these two, say, starting from Gerrard's analysis. This causes a great limitation when one studies, for example, the resonant oscillations of a drop at a certain size or the breakup of the drop due to oscillations, and so on.

The connection between the frequency of eddy detachment and the frequency of drop oscillation is rather perplexing. When the two become almost the same, resonant oscillations like those observed by Gunn[15] result. For drop sizes of smaller diameter,

both the oscillations will be acting and that which takes up the minimum energy will be more effective and hence if vortex detachment exists for these drops, then the drop will in all probability execute oscillations with this frequency. This has been the primary cause for the critical oscillations in the experimental results of Kaparthi and Licht[26]. But in most of the cases, unless the drop velocity is very large, Reynolds' number will not be large enough to permit vortex discharge and hence these forced oscillations will not be observed. For drops of large size, the natural oscillations of the drop have a relatively smaller frequency and hence they predominate. But in almost all the cases wherein the Reynolds' number is large enough to provide a periodic discharge, the oscillating pressure field makes the drop to oscillate, but the precise value of the frequency of the drop may have to be obtained as a solution of the forced oscillation problem. But this cause for the oscillation to start is not valid in all the cases, since the oscillations have been observed even when there is no vortex discharge.

Mass and heat transfer — The detailed relationship between the drop oscillations and factors like heat and mass transfer, surface tension gradients, turbulence in the velocity fields, etc., is still in a qualitative stage[6,27-30]. As indicated by Lewis and Pratt[31] the solute-solvent transfer can cause heat transfer, which in turn causes oscillations.

Surface active agents — Surface active agents are found to affect most of the flow parameters like terminal velocity, internal circulation, drop shape, etc.[5,16,32]. During the drop movement the surfactant will be continuously swept towards the rear of the droplet by convective transport, where it tends to accumulate. Thus, a concentration gradient and a surface tension gradient along the drop surface is introduced. Such a nonuniform interfacial tension can be represented by $T = \sum_{i=0}^{\infty} \alpha_i P_i (\cos\theta)$, where α_i is constant. But calculations with a general expression for T, like the present one, will be extremely difficult to make. However, nonuniform tension around the surface causes an asymmetric distortion and this combined with the viscous forces, which tend to bring the drop to equilibrium, can cause oscillations[33-35].

Large Reynolds' numbers —As Reynolds' number of the drop increases, the shape of the drop deviates from the spherical shape, and depending on the *Re* and the specifications of the phases, it attains a shape of either an oblate spheroid or a spherical cup[2,6,36]. The initial stages of the deformation have been attributed to the inertial effects[37]. But when the deformation becomes large, the drops drift in the path and sometimes follow a helical curve. This might in some cases cause oscillations[21,38-40].

Other causes — Several other factors like wall proximities, shock waves[31], nonuniform flows, method of drop production, etc., can affect drop oscillations. But these factors are not always present in the cases where oscillations are observed.

Growth and Decay of Oscillations

When once the oscillations have set in the drop, its growth or decay obviously depends on the two-phase parameters. While the viscous energies of the drop and the medium tend to damp the oscillations, the surface energy of the vibrating interface tries to restore it. Depending on whichever energy is larger, the later behaviour of oscillations results. In most of the cases, since the amplitude of oscillation will be small, the oscillations are damped down[6,7,13]. But the rate of damping differs much from that obtained by a simple analysis of the type of Lamb[41]. In several cases, the oscillations persisted for a long time without appreciable damping[42]. This may be because of a driving force being created continuously. When the amplitude of oscillation becomes quite large, often a splitting of the drop has been found to occur[43-45]. But the more common breakup of the drop results either when the drop is stripped of the sides or when it gets flattened, blows up and explodes with considerable violence[46-49]. However, drop breakup as caused by periodic oscillations is very rare.

Aperiodic damping of the surface disturbances can occur when the drop size is smaller than a critical size determined by the parameter $\hat{\rho}\hat{\nu}^2/T$. For water in air type of drops, this critical size is $\sim 10^{-6}$ cm, but for very viscous liquids of low interfacial tension, the critical size can be as large as a few millimetres. This type of damping does not seem to have been explicitly observed so far.

Oscillations of a Stationary Liquid Drop of Spherical Shape

Formulation of the Problem

The problem is basically one of solving the perturbed equations of motion for the drop and the continuous phases with matched boundary conditions. This solution is outlined in some detail below, because essentially similar techniques are used in later sections, where these details are left out.

For simplicity, the equations of motion are written in non-dimensional parameters by adopting the radius of the undeformed spherical drop a as a characteristic length, σ, which will be introduced later as a characteristic frequency and $(a^2)(a\sigma)$ as a characteristic stream function. The motion is considered to be spherically symmetric about the axis $\theta = 0$, and hence independent of ϕ. The equations of motion for the drop (labelled with a carat) and the continuous phase (no carat) can be written in the dimensionless form

$$\left.\begin{aligned} \frac{\partial}{\partial t}(D^2\Psi) + E(\Psi, \Psi) &= \frac{1}{g} D^4\Psi \\ \frac{\partial}{\partial t}(D^2\hat{\Psi}) + E(\hat{\Psi}, \hat{\Psi}) &= \frac{1}{\hat{g}} D^4\hat{\Psi} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots (3.1)$$

where g is an oscillation parameter equal to $\frac{a^2\sigma}{\nu}$,

$$\hat{g} = a^2\sigma/\hat{\nu}$$

$$D^2 = \frac{\partial^2}{\partial r^2} + \frac{1-\xi^2}{r^2}\frac{\partial^2}{\partial \xi^2}, \quad \xi = \cos\theta$$

and

$$E(\Psi, \hat{\Psi}) = \frac{1}{r^2}\left[\frac{\partial(\Psi, D^2\hat{\Psi})}{\partial(r, \xi)} + \left(\frac{2\xi}{1-\xi^2}\frac{\partial\Psi}{\partial r} + \frac{2}{r}\frac{\partial\Psi}{\partial\xi}\right)D^2\hat{\Psi}\right] \quad \ldots(3.2)$$

On the stationary drop in the fluid medium, we superimpose a perturbation which makes the drop to oscillate. Then considering the undeformed spherical drop to have unit radius (in the dimensionless units) we have as a consequence of perturbation, the drop radius

$$r = 1+\epsilon P_l(\xi) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.3)$$

where ϵ is a function of time $\epsilon_0 e^{it}$ with σ^{-1} as the unit of time. The perturbation of the drop is assumed to be small, such that ϵ_0^2, ϵ_0^3, ... can be neglected in comparison with 1. Then we can write

$$\left.\begin{aligned}\Psi &= \Delta\Psi'_0 e^{it}+\Delta\Psi''_0 e^{2it}+\Delta\Psi'''_0 e^{3it}+\ldots\\ \hat{\Psi} &= \Delta\hat{\Psi}'_0 e^{it}+\Delta\hat{\Psi}''_0 e^{2it}+\Delta\hat{\Psi}'''_0 e^{3it}+\ldots\end{aligned}\right\} \quad \ldots \quad \ldots(3.4)$$

We can substitute these values of Ψ, $\hat{\Psi}$ in Eq. (3.1) and collect the coefficients of e^{it}, e^{2it}, e^{3it}, ... to form the perturbation equations of I, II, III ... orders respectively. Then we get equations of the type

$$D^2[i\Delta\Psi'_0] = \frac{1}{g}D^4\Delta\Psi'_0 \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.5a)$$

$$D^2[2i\Delta\Psi''_0]+E(\Delta\Psi'_0, \Delta\Psi'_0) = \frac{1}{g}D^4\Delta\Psi''_0 \quad \ldots(3.5b)$$

$$D^2[2i\Delta\Psi'''_0]+E(\Delta\Psi'_0, \Delta\Psi''_0)+E(\Delta\Psi''_0, \Delta\Psi'_0) = \frac{1}{g}D^4\Delta\Psi'''_0 \quad \ldots(3.5c)$$

Similar equations can be written down for the drop phase also.

The first order perturbation equations [Eq. (3.5a) and the similar one for the drop phase] will now be analysed in detail. The calculations of Lamb and others leave out the viscous and inertial terms from this, so that one has only $(\partial/\partial t)(D^2\Psi) = 0$. In the present case even the first order equation, therefore, gives significant deviations from these calculations.

Boundary Conditions and the Characteristic Equation

Let us consider Eq. (3.5a) and the corresponding equation for the drop phase, i.e.

$$\left.\begin{aligned}D^2(D^2+h^2)\Delta\Psi'_0 &= 0\\ D^2(D^2+\hat{h}^2)\Delta\hat{\Psi}'_0 &= 0\end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(3.6)$$

where $h^2 = -ig = -i\sigma a^2/\nu$, $\hat{h}^2 = -i\hat{g} = -i\sigma a^2/\hat{\nu}$.

The contribution from the inertial terms is not present in these equations. Physically meaningful solutions can be obtained in a straightforward manner and one obtains

$$\left.\begin{aligned}\Delta\Psi'_0 &= [Br^{-l}+Dr^{\frac{1}{2}}J_{-(l+\frac{1}{2})}(hr)]F_l(\xi)\\ \Delta\hat{\Psi}'_0 &= [Ar^{l+1}+Cr^{\frac{1}{2}}J_{l+\frac{1}{2}}(\hat{h}r)]F_l(\xi)\end{aligned}\right\} \quad \ldots \quad \ldots(3.7)$$

where $F_l(\xi) = \int_{-1}^{\xi} P_l(\xi)d\xi$ are the Gegenbauer functions. A more general solution satisfying the boundary conditions would involve Hankel functions H instead of Bessel functions. But the latter have been chosen for purposes of easy computation as tables of $J_n(\chi)$ are readily available. The solutions have been chosen in such a manner so as to satisfy the conditions at $r = 0$ and $r = \infty$. The constants A, B, C and D will have to be evaluated using the boundary conditions[4,38], namely the continuity of the velocity components and those of the stress components. Hence, the interfacial conditions can be written as

$$u_r = \hat{u}_r,\ u_\theta = \hat{u}_\theta,\ T_{r\theta} = \hat{T}_{r\theta}$$

and

$$T_{rr} = \hat{T}_{rr}+\frac{2}{We}\left(\frac{1}{\chi_1}+\frac{1}{\chi_2}\right) \text{ at the interface } r = 1$$

where

$$u_r = -\frac{1}{r^2}\frac{\partial\Psi}{\partial\xi},\ u_\theta = -\frac{1}{r(1-\xi^2)^{\frac{1}{2}}}\frac{\partial\Psi}{\partial r} \quad \ldots(3.8)$$

χ_1 and χ_2 are the principal radii of curvature and $We = \rho a^3\sigma^2/T$ is the Weber number. The two velocity conditions when applied to the two phases give

$$A+CJ_{l+\frac{1}{2}}(\hat{h})-B-DJ_{-(l+\frac{1}{2})}(h) = 0 \quad \ldots \quad \ldots(3.9)$$

$$A(l+1)+C[(l+1)J_{l+\frac{1}{2}}(\hat{h})-\hat{h}J_{l+3/2}(\hat{h})]+Bl + D[lJ_{-(l+\frac{1}{2})}(h)+hJ_{-(l-\frac{1}{2})}(h)] = 0 \quad \ldots(3.10)$$

The expressions for the tangential stresses are

$$\hat{T}_{r\theta} = \frac{2\Upsilon}{\hat{g}}\left[\frac{1}{r}\frac{\partial\hat{u}_r}{\partial\theta}-\frac{\hat{u}_\theta}{r}+\frac{\partial\hat{u}_\theta}{\partial r}\right], \text{ where } \Upsilon = \hat{\rho}/\rho \quad \ldots(3.11a)$$

$$= \frac{2\Upsilon}{\hat{g}}\left[(1-\xi^2)^{\frac{1}{2}}\frac{\partial P_l}{\partial\xi}\left\{Ar^{l-2}+\frac{CJ_{l+\frac{1}{2}}}{r^{5/2}}\right\} + \frac{F_l}{(1-\xi^2)^{\frac{1}{2}}}\left\{-A(l+1)(l-2)r^{l-2} - \frac{C(l+1)(l-2)}{r^{5/2}}J_{l+\frac{1}{2}}-\frac{2C\hat{h}}{r^{3/2}}J_{l+3/2}+\frac{C\hat{h}^2}{r^{\frac{1}{2}}}J_{l+\frac{1}{2}}\right\}\right]e^{it} \quad \ldots(3.11b)$$

$$T_{r\theta} = \frac{2}{g}\left[\frac{1}{r}\frac{\partial u_r}{\partial\theta}-\frac{u_\theta}{r}+\frac{\partial u_\theta}{\partial r}\right] \quad \ldots \quad \ldots(3.12a)$$

$$= \frac{2}{g}\left[1-\xi^2)^{\frac{1}{2}}\frac{\partial P_l}{\partial\xi}\left\{\frac{B}{r^{l+3}}+\frac{D}{r^{5/2}}J_{-(l+\frac{1}{2})}\right\} - F_l\left\{\frac{Bl(l+3)}{r^{l+3}}+\frac{Dl(l+3)}{r^{5/2}}J_{-(l+\frac{1}{2})}+\frac{2Dh}{r^{3/2}}J_{-(l-\frac{1}{2})} - \frac{Dh^2}{r^{\frac{1}{2}}}J_{-(l-\frac{1}{2})}\right\}\right]e^{it} \quad \ldots \quad \ldots(3.12b)$$

The condition $\hat{T}_{r\theta} = T_{r\theta}$ at $r = 1$ gives, after differentiating with respect to ξ and rearranging,

$$\Upsilon A(l^2-1)+\Upsilon C\left[(l^2-1)J_{l+\frac{1}{2}}(\hat{h})+\hat{h}J_{l+3/2}(\hat{h})-\frac{\hat{h}^2}{2}J_{l+\frac{1}{2}}(\hat{h})\right] - \frac{B\hat{h}^2}{h^2}l(l+2)+\frac{D\hat{h}^2}{h^2}\left[-l(l+2)J_{-(l+\frac{1}{2})}(h) - hJ_{-(l-\frac{1}{2})}(h)+\frac{h^2}{2}J_{-(l+\frac{1}{2})}(h)\right] = 0 \quad \ldots \quad \ldots(3.13)$$

Similarly, the condition for the balance of radial stresses can be derived. Now

$$\hat{T}_{rr}=\hat{p}_0+\delta\hat{p}-\frac{4\Upsilon}{\hat{g}}\frac{\partial\hat{u}_r}{\partial r} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.14)$$

An expression for $\delta\hat{p}$ can be found by using the Navier-Stokes equation in the Stokes form

$$\frac{\partial\hat{u}_r}{\partial t}=-\frac{1}{2\Upsilon}\frac{\partial\delta\hat{p}}{\partial r}+\frac{1}{g}\left[\frac{\partial^2\hat{u}_r}{\partial r^2}+\frac{2}{r}\frac{\partial\hat{u}_r}{\partial r}-\frac{2\hat{u}_r}{r^2}+\frac{1-\xi^2}{r^2}\frac{\partial^2\hat{u}_r}{\partial\xi^2}-\frac{2\xi}{r^2}\frac{\partial\hat{u}_r}{\partial\xi}+\frac{2(1-\xi^2)^{\frac{1}{2}}}{r^2}\frac{\partial\hat{u}_\theta}{\partial\xi}-\frac{2\hat{u}_\theta}{r^2}\cot\theta\right]$$

This gives

$$\delta\hat{p}=2\Upsilon\frac{Ar^l}{l}ie^{it}P_l \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.15a)$$

Similarly, we have

$$\delta p=-\frac{2BP_le^{it}}{(l+1)r^{l+1}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.15b)$$

Hence, we can write

$$\hat{T}_{rr}=\hat{p}_0+2\Upsilon iA\frac{r^l}{l}P_le^{it}+\frac{4\Upsilon}{\hat{g}}\left[A(l-1)r^{l-2}+\frac{C(l-1)}{r^{5/2}}J_{l+\frac{1}{2}}-\frac{C\hat{h}}{r^{3/2}}J_{l+3/2}\right]P_le^{it} \quad \ldots \quad \ldots(3.16a)$$

and

$$T_{rr}=p_0-\frac{2BiP_le^{it}}{(l+1)r^{l+1}}-\frac{4e^{it}P_l}{g}\left[\frac{B(l+2)}{r^{l+3}}+\frac{D(l+2)}{r^{5/2}}J_{-(l+\frac{1}{2})}+\frac{Dh}{r^{3/2}}J_{-(l-\frac{1}{2})}\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.16b)$$

At the interface $r=1$, we have the condition

$$T_{rr}=\hat{T}_{rr}-\frac{2}{We}\left(\frac{1}{\chi_1}+\frac{1}{\chi_2}\right) \quad \ldots \quad \ldots \quad \ldots(3.17)$$

But

$$1/\chi_1+1/\chi_2=2+\epsilon(l-1)(l+2)P_l \text{ (Lamb}^{50}\text{, Landau and Lifshitz}^{51}\text{)} \quad \ldots(3.18)$$

An expression for ϵ can be found by using

$$r=1+\epsilon P_l=\int_0^t u_r dt=\int_0^t \hat{u}_r dt$$

$$=-\left[Ar^{l-1}+\frac{CJ_{l+\frac{1}{2}}}{r^{3/2}}\right]\frac{P_le^{it}}{i}$$

Hence

$$\epsilon=-\frac{1}{P_l}\left[Ar^{l-1}+\frac{CJ_{l+\frac{1}{2}}}{r^{3/2}}\right]\frac{e^{it}}{i} \quad \ldots \quad \ldots \quad \ldots(3.19)$$

Hence condition (3.17) can be rewritten as

$$\hat{p}_0+\frac{2\Upsilon iA}{l}P_le^{it}+\frac{4\Upsilon}{\hat{g}}[A(l-1)+C(l-1)J_{l+\frac{1}{2}}(\hat{h})-C\hat{h}J_{l+3/2}(\hat{h})]P_le^{it}-\frac{2}{We}\left[2-(l-1)(l+2)-(l-1)(l+2)(A+CJ_{l+\frac{1}{2}})\frac{P_le^{it}}{i}\right]$$

$$=p_0-\frac{2iBP_le^{it}}{l+1}-\frac{4}{g}P_le^{it}[B(l+2)+D(l+2)J_{-(l+\frac{1}{2})}+DhJ_{-(l-\frac{1}{2})}]$$

Leaving out the time independent terms, as the condition will be satisfied in the steady state, we get

$$A\left[\frac{2\Upsilon i}{l}+\frac{4\Upsilon(l-1)}{\hat{g}}+\frac{2(l-1)(l+2)}{iWe}\right]+C\left[\frac{4\Upsilon(l-1)}{\hat{g}}J_{l+\frac{1}{2}}-\frac{4\Upsilon}{\hat{g}}\hat{h}J_{l+3/2}+\frac{2(l-1)(l+2)}{iWe}J_{l+\frac{1}{2}}\right]+B\left[\frac{2i}{l+1}+\frac{4(l+2)}{g}\right]+\frac{4D}{g}[(l+2)J_{-(l+\frac{1}{2})}+hJ_{-(l-\frac{1}{2})}]=0 \quad (3.20)$$

Thus, we get the four homogeneous equations in A, B, C and D satisfying the boundary conditions. In order that they be satisfied simultaneously, the secular determinant should vanish. Hence, we get Eq. (3.21) from Eqs. (9), (10), (13) and (20).

$$\begin{bmatrix} 1 & J_{l+\frac{1}{2}}(\hat{h}) & -1 & -J_{-(l+\frac{1}{2})}(h) \\ l+1 & (l+1)J_{l+\frac{1}{2}}-\hat{h}J_{l+3/2} & l & lJ_{-(l+\frac{1}{2})}+hJ_{-(l-\frac{1}{2})} \\ \Upsilon(l^2-1) & \Upsilon\left[(l^2-1)J_{l+\frac{1}{2}}+\hat{h}J_{l+3/2}-\frac{\hat{h}^2}{2}J_{(l+\frac{1}{2})}\right] & -\frac{\hat{h}^2}{h^2}l(l+2) & \frac{\hat{h}^2}{h^2}\left[-l(l+2)J_{-(l+\frac{1}{2})}-hJ_{-(l-\frac{1}{2})}+\frac{h^2}{2}J_{-(l+\frac{1}{2})}\right] \\ \left[\frac{2\Upsilon i}{l}-\frac{4\Upsilon i(l-1)}{\hat{h}^2}+\frac{2(l-1)(l+2)}{iWe}\right] & \left[-\frac{4i\Upsilon(l-1)}{\hat{h}^2}J_{l+\frac{1}{2}}+\frac{4i\Upsilon}{\hat{h}}J_{l+3/2}+\frac{2(l-1)(l+2)}{iWe}J_{l+\frac{1}{2}}\right] & \left[\frac{2i}{l+1}-\frac{4i(l+2)}{h^2}\right] & -\frac{4i}{h^2}[(l+2)J_{-(l+\frac{1}{2})}+hJ_{-(l-\frac{1}{2})}] \end{bmatrix}=0 \quad \ldots(3.21)$$

Various Cases of Interest

(i) In the study of oscillations of a liquid drop, the parameters $\Upsilon = \hat{\rho}/\rho$, $k = \Upsilon\hat{\nu}/\nu$, $\hat{h}^2 = -i\sigma a^2/\hat{\nu}$ and $\hat{We} = \hat{\rho}a^3\sigma^2/T$ appear explicitly and the determinantal equation can be further reduced and simplified to the form

$$\left[-\sigma_{01}^2+1-\frac{2l(l-1)}{\hat{h}^2}+\frac{l}{\Upsilon(l+1)}-\frac{2l(l+2)}{k\hat{h}^2}\right]\left[-\frac{\hat{h}^3}{(\Upsilon k)^{\frac{1}{2}}}Q_{l+\frac{1}{2}}+\hat{h}^3Q_{-(l+\frac{1}{2})}-2\hat{h}^2\left(1-\frac{1}{k}\right)Q_{l+\frac{1}{2}}Q_{-(l+\frac{1}{2})}\right]$$

$$=2Q_{l+\frac{1}{2}}\frac{l\hat{h}}{(\Upsilon k)^{\frac{1}{2}}}\left[\frac{l(l+2)}{l+1}\left(1-\frac{1}{k}\right)+(2l+1)\right]$$

$$+2\hat{h}Q_{-(l+\frac{1}{2})}\left[-\frac{l(2l+1)}{k}+(l^2-1)\left(1-\frac{1}{k}\right)\right]$$

$$-2Q_{l+\frac{1}{2}}Q_{-(l+\frac{1}{2})}l\left(1-\frac{1}{k}\right)\left[-\frac{2l(l+2)}{k}+2(l^2-1)\right]$$

$$-\frac{l(2l+1)\hat{h}^2}{(\Upsilon k)^{\frac{1}{2}}(l+1)}-\frac{(2l+1)\hat{h}^2}{(\Upsilon k)^{\frac{1}{2}}} \quad \ldots \quad \ldots \quad \ldots(3.22)$$

where

$$\sigma_{01}^2=\frac{l(l-1)(l+2)}{\hat{We}};\quad Q_{l+\frac{1}{2}}(\hat{h})=\frac{J_{l+3/2}(\hat{h})}{J_{l+\frac{1}{2}}(\hat{h})}$$

$$Q_{-(l+\frac{1}{2})}(h)=\frac{J_{-(l-\frac{1}{2})}(h)}{J_{-(l+\frac{1}{2})}(h)} \quad \ldots \quad \ldots \quad \ldots(3.23)$$

σ_{01} corresponds to the oscillation frequency of the drops in the absence of viscous forces. For the oscillation of a liquid drop in free space, $\Upsilon\to\infty$ and $k\to\infty$. Eq. (3.23) becomes

$$-\sigma_{01}^2=\frac{2(l^2-1)}{\hat{h}^2-2\hat{h}Q_{l+\frac{1}{2}}}+\frac{2l(l-1)}{\hat{h}^2}\left[1-\frac{(l+1)Q_{l+\frac{1}{2}}}{\hat{h}/2-Q_{l+\frac{1}{2}}}\right]-1 \quad \ldots(3.24)$$

a result already obtained by Reid[52,53].

(ii) For the study of oscillations of a bubble, the variables Υ, k, h and We are to be used. In this case, the determinantal Eq. (3.21) simplifies to

$$\left[-\sigma_{02}^2+\frac{\Upsilon(l+1)}{l}-\frac{2k(l-1)(l+1)}{h^2}+1-\frac{2(l+1)(l+2)}{h^2}\right]$$

$$\times[-h^3Q_{l+\frac{1}{2}}+(\Upsilon k)^{\frac{1}{2}}h^3Q_{-(l+\frac{1}{2})}-2(k-1)h^2Q_{l+\frac{1}{2}}Q_{-(l+\frac{1}{2})}]$$

$$=2Q_{l+\frac{1}{2}}(l+1)h\left[\frac{l(l+2)}{l+1}(k-1)+(2l+1)k\right]$$

$$+2Q_{-(l+\frac{1}{2})}(\Upsilon k)^{\frac{1}{2}}h\frac{(l+1)}{l}[-l(2l+1)+(l^2-1)(k-1)]$$

$$-2Q_{l+\frac{1}{2}}Q_{-(l+\frac{1}{2})}(k-1)(l+1)[-2l(l+2)+2k(l^2-1)]$$

$$-(2l+1)^2\frac{\Upsilon kh^2}{2l} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.25)$$

where $\sigma_{02}^2=\dfrac{(l-1)(l+1)(l+2)}{We}$, σ_{02} being the oscillation frequency of the bubble in the absence of viscous forces. For the oscillation of a bubble in a dense and viscous liquid, $\Upsilon\to 0$ and $k\to 0$. Then Eq. (3.25) can be rewritten as

$$-\sigma_{02}^2=\frac{2(l+1)(l+2)}{h^2}+\frac{2l(l+2)}{h^2-2hQ_{-(l+\frac{1}{2})}}\times\left[1+\frac{2}{h}(l+1)Q_{-(l+\frac{1}{2})}\right]-1 \quad \ldots(3.26)$$

Eq. (3.26) has been derived only for incompressible fluids and proper care should be taken when applying it to oscillations of bubbles.

(iii) The oscillation of a drop or bubble in a medium of the same density and viscosity is very interesting. When $\Upsilon = k = 1$, by writing

$$\sigma_{03}^2=\frac{l(l-1)(l+1)(l+2)}{(2l+1)\hat{We}};\ h=\hat{h}$$

we have

$$\sigma_{03}^2=1-\frac{2l+1}{h[Q_{l+\frac{1}{2}}-Q_{-(l+\frac{1}{2})}]} \quad \ldots \quad \ldots \quad \ldots(3.27)$$

Aperiodic Damping Modes of a Drop in Free Space

Depending upon the choice in the practical case, one of the equations (3.22), (3.25), (3.27) or the limiting equations can be used to determine the frequency. However, these equations have the frequency σ as an implicit parameter, since it appears both in σ_0 and in h or $\hat{h}$ as the case may be. Also σ is a complex number deciding both the frequency and the damping factor. This makes these equations more complicated and they will have to be split into real and imaginary parts to find the frequency and the damping factor.

Let us first consider Eq. (3.24), which gives the frequencies of oscillation of a drop in free space. This equation has been studied by Chandrasekhar and Reid for the aperiodic damping modes, i.e. σ to be purely negative and imaginary. In such a case, it can be shown easily that the damping constant σ increases with increase in $(\sigma_{\text{Lamb}}a^2/\hat{\nu})$, reaches a maximum and then folds on to itself, giving a different set of values of σ for the same $\sigma_L a^2/\hat{\nu}$ and finally goes over to infinity for $\sigma_L a^2/\hat{\nu}\to 0$ (Fig. 2). Thus, below a critical value of $\sigma_L a^2/\hat{\nu}$ (which determines a critical radius of the drop a_c), there are two damping modes possible and, in practice, the lower of the two predominates because of energy considerations. The value of a_c is that required for the oscillations to start and all drops of sizes smaller than a_c should not execute any prolate-oblate oscillation at all. The value of a_c, which will be very small in most of the cases, can account for the non-observance of oscillations in, say, drops or bubbles in very viscous liquids. This will be considered in some more detail at a later stage. (In the calculations of Chandrasekhar and Reid on oscillations of water drops in air, $\sigma_L a^2/\hat{\nu} = 3{\cdot}69$, thus giving the value $a_c = 2{\cdot}34\times10^{-6}$ cm and not $2{\cdot}3\times10^{-2}$ cm as reported by them.)

In addition to these lowest aperiodic damping modes, there are infinite number of higher damping modes with larger damping constants which are not of practical importance.

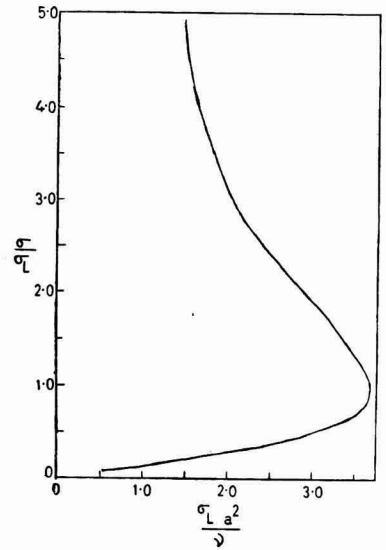

Fig. 2 — Aperiodic damping modes of a drop in free space ($\gamma \to \infty$; $k \to \infty$)

Oscillatory Modes of a Drop in Free Space

If the size of the drop exceeds the critical size a_c, then the decay modes must be characterized by complex σ with a damping part. A complete numerical analysis of the corresponding characteristic equation is difficult because of the lack of tables of spherical Bessel functions with complex arguments. A partial analysis of the oscillations of a drop in free space will be taken up presently.

Since σ is a complex quantity, it can be written as $\sigma = \sigma_r + i\sigma_i$, where σ_r and σ_i are the real and imaginary parts. Then

$$\hat{h}^2 = -i\sigma a^2/\nu = \alpha^2(\beta - i) \quad \ldots \quad \ldots \quad \ldots(3.28)$$

where

$$\alpha^2 = \sigma_r a^2/\nu, \ \beta = \sigma_i/\sigma_r \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.29)$$

Hence

$$\hat{h} = \pm\alpha/\sqrt{2}\,[\{\beta \pm (\beta^2+1)^{\frac{1}{2}}\}^{\frac{1}{2}} - i\{\beta \pm (\beta^2+1)^{\frac{1}{2}}\}^{-\frac{1}{2}}]$$
$$= \pm\alpha/\sqrt{2}\,[(1+\tfrac{1}{2}\beta) - i(1-\tfrac{1}{2}\beta)] \quad \ldots \quad \ldots(3.30)$$

since β is usually much less than unity.

The range of values of α and β in practical cases can be obtained very easily. Since $\alpha^2 = \sigma_r a^2/\nu$ (σ_r, the frequency of oscillation can be approximated, for this purpose by Lamb's expression), $\alpha > 0(10)$, except in highly viscous liquids when it can be 0(1). The damping factor σ_i is much less than σ_r to give $\beta < 0(1)$. In these ranges of α and β, expressions for Bessel functions can be simplified to a large extent as, for example, shown in Appendix 1 whence we get

$$Q_{5/2}(\hat{h}) = \frac{6(1+\frac{1}{2}\beta) + 6i(1-\frac{1}{2}\beta) - i\sqrt{2}\alpha}{\sqrt{2}\alpha - 3(1-\frac{1}{2}\beta)} + O\left(\frac{1}{\alpha^2}, \beta^2\right) \quad \ldots(3.31)$$

$$Q_{-3/2}(\hat{h}) = \frac{-\sqrt{2}(1+\frac{1}{2}\beta) - i\alpha + 2\sqrt{2}i(1-\frac{1}{2}\beta)}{\alpha - 3\sqrt{2}(1-\frac{1}{2}\beta)} + O\left(\frac{1}{\alpha^2}, \beta^2\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots(3.32)$$

where $Q_{5/2} = J_{7/2}/J_{5/2}$, $Q_{-3/2} = J_{-3/2}/J_{-5/2}$, $l = 2$.

The method of calculation of the dependence of σ on drop parameters is as follows. Any pair of values (α, β) is chosen. Then $Q_{5/2}$, and hence σ_{01}^2, can be calculated from Eqs. (3.31) and (3.24) respectively. Since

$$\sigma_{01}^2 = \frac{l(l-1)(l+2)}{\hat{We}} = \frac{8T}{\rho a^3 \sigma_r^2}$$

for $l = 2$, we get the value of σ_L^2/σ_r^2 for a given $\alpha^2 = \sigma_r a^2/\nu$, $\beta = \sigma_i/\sigma_r$. Hence, one can find σ_L/σ_r and σ_i/σ_r as functions of $\sigma_L a^2/\nu$. But the choice of α, β cannot be made indiscriminately, as it otherwise would lead to an infinite number of σ's for a given system. This may be avoided if we separate Eq. (3.24) into real and imaginary parts and this gives a proper relation between α and β. However, an accurate relation between α and β is very difficult to find even in this way and an approximate relation is derived in Appendix 2. For the case $\Upsilon \to \infty$, $k \to \infty$, $l = 2$

$$\beta \simeq 5/\alpha^2 \text{ for } Q_{5/2} \text{ positive} \quad \ldots \quad \ldots \quad \ldots(3.33)$$

β is positive, showing the damping of the oscillations as is to be expected. Another possibility would be to take $Q_{5/2}$ negative, as this is in no way wrong and even in this case, we continue to get

$$\beta' \simeq 5/\alpha^2 \text{ for } Q_{5/2} \text{ negative} \quad \ldots \quad \ldots \quad \ldots(3.34)$$

β' being still positive.

Then a series of values of α, β satisfying Eq. (3.33) can be chosen and computation carried out giving σ_r and σ_i as functions of the drop parameters (Table 1). The two values of frequency of oscillation caused by the alternate signs of $Q_{5/2}$ do not differ much from Lamb's frequency in this limiting case of a drop oscillating in free space.

Before considering the numerical results of the oscillations of a liquid drop in a fluid medium, it is worth while considering the other two asymptotic cases of the oscillations of a bubble in a dense viscous liquid and those of a fluid sphere in a medium of the same viscosity.

Aperiodic Damping Modes of a Bubble in a Dense Viscous Liquid

Eq. (3.26) describes the oscillatory and the damping modes for the case $\Upsilon \to 0$, $k \to 0$. We shall first consider the aperiodic damping modes, if there are any, by taking σ to be purely imaginary. Then Eq. (3.26) can be recast in the form

$$\frac{h^4\sigma_L^2}{\sigma^2} = \frac{\sigma_L^2 a^4}{\hat{\nu}^2} = 24h^2 + \frac{16h^2(1+6Q_{-3/2}/h)}{h^2 - 2hQ_{-3/2}} - h^4 \quad \ldots(3.35)$$

where $Q_{-3/2}(h) = J_{-3/2}/J_{-5/2}$.

The calculated values of σ/σ_L are plotted against $\sigma_L a^2/\nu$ in Fig. 3. From this it appears that the

TABLE 1 — OSCILLATIONS OF A LIQUID DROP IN FREE SPACE

$(\gamma \to \infty\,;\, k \to \infty)$

α	β	σ_L^2/σ_r^2	σ_r/σ_L	β'	$\sigma_L^2/\sigma_r'^2$	σ_r'/σ_L
10	0·05	$1{\cdot}0125-0{\cdot}039i$	0·9940	0·05	$1{\cdot}0019+0{\cdot}004i$	0·9982
50	0·002	$1{\cdot}0001-2\times10^{-4}i$	~1	0·002	$0{\cdot}9999+2\times10^{-4}i$	~1
100	0·0005	$1-10^{-5}i$	~1	0·0005	$1{\cdot}0022-0{\cdot}063i$	0·999
1000	~0	$1+10^{-5}i$	~1	~0	$1+25\times10^{-9}i$	~1

TABLE 2 — DAMPED OSCILLATIONS OF A BUBBLE IN A DENSE VISCOUS LIQUID

$(\gamma \to 0\,;\; k \to 0)$

α	β	σ_L^2/σ_r^2	σ_r/σ_L	β'	$\sigma_L^2/\sigma_r'^2$	σ_r'/σ_L
20	0·08	$1{\cdot}0014+0{\cdot}0438i$	0·9991	0·05	$0{\cdot}998-0{\cdot}04i$	1·001
50	0·0087	$0{\cdot}9992+0{\cdot}013i$	~1	0·008	$1{\cdot}001+0{\cdot}002i$	~1
100	0·0021	$0{\cdot}9999+10^{-4}i$	~1	4×10^{-4}	$1+10^{-4}+10^{-3}i$	~1
1000	~0	1·0000	~1	~0	1	~1

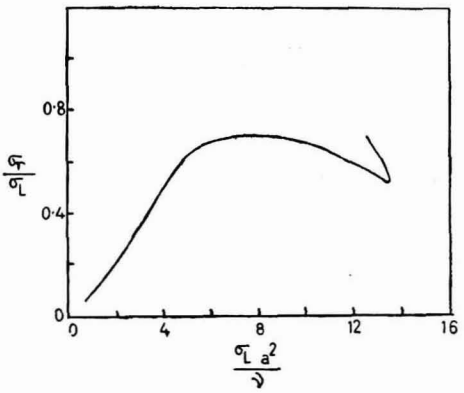

Fig. 3 — Aperiodic damping modes of a bubble in a dense viscous liquid $(\gamma \to 0\,;\; k \to 0)$

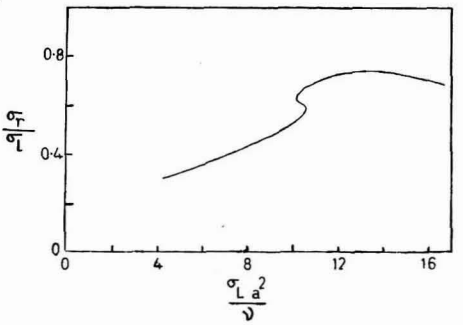

Fig. 4 — Aperiodic damping of a drop in a similar fluid $(\gamma = 1\,;\; k = 1)$

damping constant increases continuously with the drop size without approaching any critical size as in the last case. This does not mean that the aperiodic damping mode exists for all drop sizes, but it is merely because of the singular behaviour of $(h^2-2hQ_{-3/2})^{-1}$ in this approximation. Such a situation arose even in the last case of $\gamma\to\infty$, $k\to\infty$ for higher damping modes. Considering only the first turning point in the figure, an approximate value of the critical size can be given by $\sigma_L a^2/\nu \simeq 10{\cdot}6$, which gives the critical size for oscillations to start as $a_c \simeq 5\times10^{-5}$ cm for a system such as an air bubble in water.

Oscillatory Damping Modes of a Bubble in a Dense Viscous Liquid

As in the previous case, σ can be taken to be a complex number. Then

$$h = \pm\frac{\alpha}{\sqrt{2}}[(1+\tfrac{1}{2}\beta)-i(1-\tfrac{1}{2}\beta)] \quad \ldots \quad \ldots(3.36)$$

where $\alpha^2 = \sigma_r a^2/\nu$, $\beta = \sigma_i/\sigma_r$.

An expression for $Q_{-3/2}$ is given by Eq. (3.32) and the relation between α and β can be obtained as before. This has been done in Appendix 2 giving

$$\left.\begin{aligned}\beta &= \frac{20}{\alpha^2}\,\frac{\alpha-8\sqrt{2}}{\alpha-10\sqrt{2}} \text{ for } Q_{-3/2} \text{ positive}\\ \beta' &= \frac{4}{\alpha^2}\,\frac{5\alpha-8\sqrt{2}}{\alpha-2\sqrt{2}} \text{ for } Q_{-3/2} \text{ negative}\end{aligned}\right\} \quad \ldots(3.37)$$

Both β and β' are allowed as they damp the oscillations. Here again the variation of the frequency of oscillation on the drop parameters can be studied.

It is seen from the data presented in Table 2 that in this limiting case also, these values are almost the same as those given by Lamb.

Damping and Oscillatory Modes for $\gamma = 1$, $k = 1$

The aperiodic damping modes are discussed as in the last case with the help of the equation

$$-\frac{\sigma_L^2}{\sigma_r^2} = 1 - \frac{5}{h(Q_{5/2}-Q_{-3/2})} \quad \ldots \quad \ldots \quad \ldots(3.38)$$

The numerical values of σ_L/σ_r are plotted against $\sigma_L a^2/\nu$ in Fig. 4. Here again the presence of a

critical size above which oscillations start is apparently not seen. This is because of the singular behaviour of $[Q_{5/2}(\hat{h})-Q_{-3/2}(\hat{h})]^{-1}$. But an approximate value of the critical size can be estimated by taking $\sigma_L a^2/\nu = 13{\cdot}5$ giving $a_c \simeq 10^{-4}$ cm.

The damped oscillations in this case are of practical importance, since in most of the liquid-liquid systems the two densities and viscosities are of comparable magnitude. As in the previous cases $h = \hat{h}$ can be split into real and imaginary parts by writing $\sigma = \sigma_r + i\sigma_i$, giving

$$h = \hat{h} = \pm\frac{\alpha}{\sqrt{2}}[(1+\tfrac{1}{2}\beta)-i(1-\tfrac{1}{2}\beta)]$$

where $\alpha^2 = \sigma_r a^2/\nu$, $\beta = \sigma_i/\sigma_r$.

The relation between α and β is found by writing the real and imaginary parts of Eq. (3.27) and is shown in Appendix 2 to be of the form:

$$\beta_1 = \frac{2\alpha-9\sqrt{2}}{4{\cdot}4\alpha+82{\cdot}5\sqrt{2}} \text{ when } Q_{5/2},\ Q_{-3/2} \text{ are both taken as positive}$$

$$\beta_2 = \frac{10}{32\alpha}\,\frac{2\sqrt{2}\alpha-33}{\alpha-9\sqrt{2}} \text{ when } Q_{5/2} \text{ is positive, but } Q_{-3/2} \text{ is negative}$$

$$\beta_3 = \frac{9\sqrt{2}-2\alpha}{40\alpha-82{\cdot}5\sqrt{2}} \text{ if both } Q_{5/2} \text{ and } Q_{-3/2} \text{ are taken as negative}$$

and

$$\beta_4 = \frac{9\sqrt{2}-2\alpha}{4\alpha(0{\cdot}4\alpha-1)} \text{ if } Q_{5/2} \text{ is negative and } Q_{-3/2} \text{ is positive}$$

For the values of α found in practice ($\gtrsim 10$), β_1 and β_2 turn out to be positive, revealing the damping nature of the oscillations, whereas β_3 and β_4 become negative and refer to the instability of the drop. For various values of α, β_1 and α, β_2 the frequencies and damping factors are computed and the results are given in Table 3. The magnitudes of the two oscillation frequencies for any drop size differ very much from Lamb's frequency. One of the frequencies is less by as much as 10-15%, whereas the other mode is larger by 20-30% (Fig. 5). In most of the observed free oscillations of the drop, the lower frequency mode will be excited because the system favours a state of minimum energy. Indeed this is exactly what has been observed, for example, by Schroeder and Kintner (16·33% less than σ_L), 25-35% deviation by Winnikow and Chao[13], 10-15% deviation by Schoessaw and Boumeister[7] and others. The mode with a higher frequency has been reported by Valentine *et al.*[42] under rather special circumstances and they observed an excess of 20-40% over Lamb's calculations.

Oscillations of a Liquid Drop in a Fluid Medium: Some Typical Numerical Results

A detailed analysis of a system which has a direct relevance to practical work can now be carried out

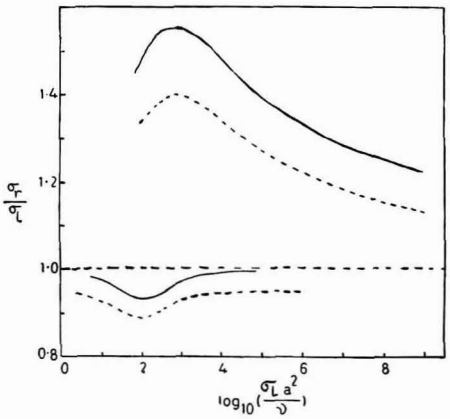

Fig. 5 — Oscillation modes of a drop in a similar fluid [($\gamma \to 1$; $k \to 1$; ——, spherical drop; - - -, deformed drop; and $\epsilon_1 = 0{\cdot}2$]

TABLE 3 — DAMPED OSCILLATIONS OF A FLUID DROP IN A SIMILAR FLUID

($\gamma = 1$; $k = 1$)

α	β	σ_L^2/σ_r^2	σ_r/σ_L		$\sigma_L^2 \frac{a^4}{\nu^2} = \alpha^4 \frac{\sigma_L^2}{\sigma_r^2}$
			Sph. drop ($\epsilon_1=0$)	Deformed drop ($\epsilon_1=0{\cdot}2$)	
10	0·0453	$0{\cdot}4751-0{\cdot}023i$	1·451	1·318	$4{\cdot}75\times10^3$
25	0·1644	$0{\cdot}4124-0{\cdot}014i$	1·553	1·396	$1{\cdot}632\times10^5$
50	0·2592	$0{\cdot}4184+0{\cdot}0446i$	1·546	1·389	$2{\cdot}617\times10^6$
100	0·3364	$0{\cdot}4453+0{\cdot}1024i$	1·498	1·357	$4{\cdot}45\times10^7$
500	0·4261	$0{\cdot}5293+0{\cdot}0838i$	1·375	1·260	$3{\cdot}309\times10^{10}$
α	β'	σ_L^2/σ_n^{12}	σ_r'/σ_L		$\sigma_L^2 \frac{a^4}{\nu^2} = \alpha^4 \frac{\sigma_L^2}{\sigma_r^2}$
			Sph. drop ($\epsilon_1=0$)	Deformed drop ($\epsilon_1=0{\cdot}2$)	
10	0·054	$1{\cdot}1647-0{\cdot}0822i$	0·9264	0·8896	$1{\cdot}165\times10^4$
25	0·069	$1{\cdot}075+0{\cdot}069i$	0·9642	0·9223	$4{\cdot}257\times10^5$
50	0·0658	$1{\cdot}0208+0{\cdot}09022i$	0·9897	0·9445	$6{\cdot}381\times10^6$
100	0·0045	$1{\cdot}0177-0{\cdot}0089i$	0·9913	0·9458	$1{\cdot}018\times1^8$
1000	0·0004	$1{\cdot}0018+0{\cdot}001i$	0·9991	0·9526	$1{\cdot}002\times10^{12}$

TABLE 4 — DAMPED OSCILLATIONS OF *o*-NITROTOLUENE DROP IN WATER

($\gamma = 1{\cdot}160$, $k = 2{\cdot}7526$, $l = 2$, $T = 26{\cdot}6$ dynes cm^{-1})

α	β	σ_L^2/σ_r^2	σ_r/σ_L	a cm
15	0·0070	$0{\cdot}7508+0{\cdot}064i$	1·154	0·1464
25	0·0068	$0{\cdot}8054+0{\cdot}077i$	1·114	1·461
50	0·0024	$0{\cdot}9035+0{\cdot}076i$	1·052	21·74
100	0·0006	$0{\cdot}9546+0{\cdot}0414i$	1·024	367·4
α	β'	$\sigma_L'^2/\sigma_r'^2$	σ_r'/σ_L	a cm
15	0·0062	$1{\cdot}2576+0{\cdot}10^{6}i$	0·8917	0·2452
25	0·0084	$1{\cdot}179-0{\cdot}086^{9}i$	0·9206	1·797
50	0·0035	$1{\cdot}0952-0{\cdot}064i$	0·9554	26·3
100	0·0010	$1{\cdot}0482-0{\cdot}0394i$	0·9768	403·5

using Eq (3.22). Because of the highly involved computations, results have been obtained only for a typical case like an *o*-nitrotoluene drop oscillating in water. To determine the nature of the damped oscillations, σ will have to be taken as a complex quantity and α, β will have to be introduced as before. The relation between α and β can be approximately worked out and then the frequency of oscillation can be computed. The results are presented in Table 4. Here again we observe the two frequency modes, one higher and the other lower than Lamb's mode.

Higher Order Solutions

Once the complete solutions of the first order perturbation equations (3.5a) are known, the solutions of equations like (3.5b), (3.5c), etc., can be found by a method of iteration[54-56]. For example, Eq. (3.5b) and its counterpart for the drop phase can be written as

$$D^2(D^2+2h^2)\Delta\Psi_0''=gE(\Delta\Psi_0', \Delta\Psi_0')$$
$$D^2(D^2+2\hat{h}^2)\Delta\hat{\Psi}_0''=\hat{g}E(\Delta\hat{\Psi}_0', \Delta\hat{\Psi}_0')$$

The expressions for $\Delta\Psi_0'$, $\Delta\hat{\Psi}_0'$ have already been derived [Eq. (3.7)]. Hence, the above equations can be solved in principle to satisfy the required set of boundary conditions. However, in view of the complex nature of even the first order solutions, a discussion of these equations has not been taken up.

Oscillations of a Deformed Drop at Rest

The study of oscillations of a fluid sphere had been confined in the last section to that with a spherical shape. This was done mainly to simplify the mathematical computations and to illustrate the techniques involved in the solution. However, in practice, the drop shape remains spherical only at very low Reynolds' numbers[57]. As the Reynolds' number increases, the drop deforms more from the spherical shape into an oblate spheroidal shape and then into a spherical cup shape[5,37,58]. Often the drop distortion does not fit into any one of the above cases and appears more approximately as two half ellipsoids of revolution with common major and differing minor axes, i.e. the horizontal symmetry is lost[59]. Sometimes the drop shape becomes too irregular to be described by simple mathematical terms. Attempts have been made by Saito[60], Harmathy[14], Elzinga and Banchero[16], Taylor and Acrivos[38] and others to find the deviation from spherical shape as a function of flow parameters. The theoretical investigations of Taylor and Acrivos, which are an improvement over Saito's work, use singular perturbation technique to solve the axisymmetric equations of motion. At low Weber numbers, the drop is deformed into an oblate spheroid

$$r = 1+\epsilon_1 P_2(\xi) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4.1)$$

where

$$\epsilon_1 = -\frac{We}{4(k+1)^3}\left[\left(\frac{81}{80}k^3+\frac{57}{20}k^2+\frac{103}{40}k+\frac{3}{4}\right) - \frac{\gamma-1}{12}(k+1)\right]$$

and then with a further increase in Weber number, the geometry approaches a spherical cup, given by

$$r = 1+\epsilon_1 P_2(\xi)+\epsilon_2\frac{We}{Re}P_3(\xi) \quad \ldots \quad \ldots \quad \ldots(4.2)$$

where

$$\epsilon_2 = \frac{3\epsilon_1(11k+10)We}{70(k+1)}$$

These equations do not fully explain many of the experimental results at high Weber and Reynolds' numbers[37,61]. But at small values of *We* and *Re*, they satisfactorily explain the observed shapes of the drops. Further, they are the best calculations available so far and, therefore, form the basis for our study of the effect of deformation on oscillation of the drop. We, therefore, consider the drop to be an oblate spheroid represented by Eq. (4.1), the deformation being caused essentially by inertial effects.

Basic Equations

The equations of motion for Stokes flow in the dimensionless form can be written as

$$\left.\begin{aligned}\frac{\partial}{\partial t}(D^2\Psi)&=\frac{1}{g}D^4\Psi \text{ for } 1\leqslant r\leqslant\infty\\ \frac{\partial}{\partial t}(D^2\hat{\Psi})&=\frac{1}{\hat{g}}D^4\hat{\Psi} \text{ for } 0\leqslant r\leqslant 1\end{aligned}\right\} \quad \ldots \quad \ldots(4.3)$$

where the oscillation parameter $g = a^2\sigma/\nu$, $\hat{g} = a^2\sigma/\hat{\nu}$. The superimposition of a perturbation on the drop interface can be written as

$$r = 1+\epsilon_1 P_2(\xi)+\epsilon P_l e^{it}(1+\epsilon_1 P_2) \quad \ldots \quad \ldots \quad \ldots(4.4)$$
$$\simeq 1+\epsilon_1 P_2+\epsilon e^{it}P_l, \text{ since } \epsilon_1, \epsilon \text{ are small}$$

Terms involving time have been made dimensionless by taking σ^{-1} as a characteristic time. Then

$$\left.\begin{aligned}\Psi &= \Psi_0+\Delta\Psi_1 e^{it}+\ldots\\ \hat{\Psi} &= \hat{\Psi}_0+\Delta\hat{\Psi}_1 e^{it}+\ldots\end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(4.5)$$

Substituting these in the equations of motion (4.3), the various ordered perturbation equations can be

written. Written explicitly they are

$$\left.\begin{aligned} D^4\Psi_0 &= 0 \\ D^4\hat{\Psi}_0 &= 0 \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4.6)$$

$$\left.\begin{aligned} D^2(D^2+h^2)\Delta\Psi_1 &= 0; \quad h^2 = -i\sigma a^2/\nu \\ D^2(D^2+\hat{h}^2)\Delta\hat{\Psi}_1 &= 0; \quad \hat{h}^2 = -i\sigma a^2/\hat{\nu} \end{aligned}\right\} \quad \ldots(4.7)$$

$$\left.\begin{aligned} D^2(D^2+2h^2)\Delta\Psi_2 &= 0 \\ D^2(D^2+2\hat{h}^2)\Delta\hat{\Psi}_2 &= 0 \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(4.8)$$

and so on.

Eqs. (4.6) are those for steady creeping flow. The first and second ordered perturbation equations are represented by Eqs. (4.7) and (4.8) respectively. In the first order equations (4.7), h^2 is a characteristic parameter depending on the viscosity.

First Order Perturbation Equations: Nonviscous Case

The equations of motion are represented by Eq. (4.7) with h, $\hat{h}\to\infty$; i.e.

$$D^2\Delta\Psi_1 = 0, \quad D^2\Delta\hat{\Psi}_1 = 0 \quad \ldots \quad \ldots \quad \ldots(4.9)$$

These are the starting equations of Lamb, but here we study, in addition, the effect of the deformed shape of the drop on the frequency of oscillation. The non-singular solutions of these equations are

$$\left.\begin{aligned} &\Delta\Psi_1 = Br^{-l}F_l e^{it} \\ &\text{and} \\ &\Delta\hat{\Psi}_1 = Ar^{l+1}F_l e^{it} \end{aligned}\right\} \quad \ldots \quad \ldots \quad \ldots(4.10)$$

The velocity components are then given by

$$\left.\begin{aligned} u_r &= -Br^{-(l+2)}P_l e^{it} \\ \hat{u}_r &= -Ar^{l-1}P_l e^{it} \\ u_\theta &= Blr^{-(l+2)}F_l e^{it}/\sin\theta \\ \hat{u}_\theta &= -A(l+1)r^{l-1}F_l e^{it}/\sin\theta \end{aligned}\right\} \quad \ldots \quad \ldots(4.11)$$

The pressure terms can also be calculated as before

$$\delta p = -\frac{BP_l e^{it}}{(l+1)r^{l+1}}; \quad \delta\hat{p} = \frac{\Upsilon Ar^l P_l e^{it}}{l} \quad \ldots(4.12)$$

Then the following conditions at the interface $r = 1+\epsilon_1 P_2$ can be used:

(i) The radial component of the velocity must be compatible with the assumed form of the deformed boundary; i.e.

$$u_r = \hat{u}_r = \partial r/\partial t \text{ at } r = 1+\epsilon_1 P_2 \quad \ldots \quad \ldots(4.13)$$

Hence

$$-BP_l e^{it}[1-(l+2)\epsilon_1 P_2] = -AP_l e^{it}[1+(l-1)\epsilon_1 P_2] = i\epsilon P_l e^{it}$$

or

$$\left.\begin{aligned} B &= -i\epsilon[1+(l+2)\epsilon_1 P_2] \\ A &= -i\epsilon[1-(l-1)\epsilon_1 P_2] \end{aligned}\right\} \quad \ldots \quad \ldots(4.14)$$

(ii) The radial component of the stresses must be continuous

$$\delta p = \delta\hat{p} - \frac{2}{We}\left(\frac{1}{\chi_1}+\frac{1}{\chi_2}\right) \quad \ldots \quad \ldots \quad \ldots(4.15)$$

where $We = (\rho a)(a^2)/T$ is the Weber number. This equation gives, after substituting for B and A

$$\frac{\Upsilon(l-1)(l+2)l(l+1)}{\hat{We}(1+\epsilon_1 P_2)} = \Upsilon(l+1)+l$$

Using the frequency of oscillation, σ_L, in the absence of deformation, as given by Lamb, i.e.

$$\sigma_L^2 = \frac{l(l-1)(l+1)(l+2)}{\hat{We}\,[l+1+(l/\Upsilon)]} \quad \ldots \quad \ldots \quad \ldots(4.16)$$

we can write

$$\sigma^2 = \frac{l(l-1)(l+1)(l+2)}{\hat{We}\,[l+1+(l/\Upsilon)]}\,(1-\epsilon_1 P_2) = \sigma_L^2(1-\epsilon_1 P_2) \quad \ldots(4.17)$$

ϵ_1, the amplitude of deviation from spherical shape enters into the equation for oscillation as just a correction term. But the oscillatory behaviour is only an average over the whole drop, and so the average value of P_2 (cos θ) will have to be used in this expression. Hence

$$\sigma^2 = \frac{l(l-1)(l+1)(l+2)}{\hat{We}\,[l+1+(l/\Upsilon)]}\left(1-\frac{\epsilon_1}{4}\right) \quad \ldots \quad \ldots(4.18)$$

or

$$\sigma^2 = b^{1/3}\sigma_L^2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4.19)$$

where b is the deformation dependent coefficient defined by

$$b = 1-\frac{d_{\max}-d_{\min}}{2d_{\text{av.}}} \simeq 1-\frac{3\epsilon_1}{4} \simeq \left(1-\frac{\epsilon_1}{4}\right)^3 \quad \ldots(4.20)$$

For almost spherical drop, $b \simeq 1$.

Using Eq. (4.19), the modified frequency caused by the deformation can be computed. For example, for the case of a water drop oscillating in air[7],

$$\left.\begin{aligned} &\sigma/\sigma_L \simeq 0{\cdot}9 \quad \text{if} \quad \epsilon_1 \simeq 0{\cdot}8 \\ &\text{and} \\ &\sigma/\sigma_L \simeq 0{\cdot}837 \quad \text{if} \quad \epsilon_1 \simeq 1{\cdot}3 \end{aligned}\right\} \quad \ldots \quad \ldots(4.21)$$

The deformations of the drop in these experiments[7] were of the same order as given by ϵ_1 above. The resulting frequencies favourably agree with the experimental results. However, this result has the obvious limitations as in Lamb's case, namely that it holds good only for inviscid case, for low Reynolds' number, low Weber number flows and small deviations from spherical shape. However, the deduction of a qualitative deviation from Lamb's result in accordance with experimental results is worth noticing.

First Order Perturbation Equation with Viscous Effects Included

In this case, Eqs. (4.7) are to be solved. Non-singular solutions can be obtained as before. They are

$$\left.\begin{aligned} \Delta\Psi_1 &= [Br^{-l}+Dr^{1/2}J_{-(l+\frac{1}{2})}(hr)]F_l(\xi)e^{it} \\ \Delta\hat{\Psi}_1 &= [Ar^{l+1}+Cr^{1/2}J_{l+\frac{1}{2}}(\hat{h}r)]F_l(\xi)e^{it} \end{aligned}\right\} \quad \ldots(4.22)$$

As in the section 'Oscillations of a Stationary Liquid Drop of Spherical Shape', the velocity components and the stress components can be calculated. Then the conditions at the boundary $r = 1+\epsilon_1 P_2$ can be written down. To simplify calculations, relations of the type

$$(\hat{u}_r)_{r=1+\epsilon_1 P_2} = \left(\hat{u}_r+\epsilon_1 P_2\frac{\partial\hat{u}_r}{\partial r}\right)_{r=1}$$

can be used. Finally, one gets for the condition $\hat{u}_r = u_r$ at $r = 1+\epsilon_1 P_2$

$$-A[1+(l-1)\epsilon_1 P_2]-C[J_{l+\frac{1}{2}}+(l-1)\epsilon_1 P_2 J_{l+\frac{1}{2}} -\epsilon_1 P_2 \hat{h} J_{l+3/2}]+B[1-(l+2)\epsilon_1 P_2]+D[J_{-(l+\frac{1}{2})} -(l+2)\epsilon_1 P_2 J_{-(l+\frac{1}{2})}-\epsilon_1 P_2 \hat{h} J_{-(l-\frac{1}{2})}] = 0 \quad \ldots(4.23)$$

Similarly, $\hat{u}_\theta = u_\theta$ at $r = 1+\epsilon_1 P_2$ gives

$$A[1+\epsilon_1 P_2(l-1)](l+1)+C[(l+1)J_{l+\frac{1}{2}}-\hat{h} J_{l+3/2} -(l+1)(l+2)\epsilon_1 P_2 J_{l+\frac{1}{2}}+\hat{h}^2 \epsilon_1 P_2 J_{l+\frac{1}{2}}] +B[1-(l+2)\ \epsilon_1 P_2]+D[l J_{-(l+\frac{1}{2})}+\hat{h} J_{-(l-\frac{1}{2})} -l(l+2)\epsilon_1 P_2 J_{-(l+\frac{1}{2})}+\hat{h}^2 \epsilon_1 P_2 J_{-(l+\frac{1}{2})} -\hat{h}\epsilon_1 P_2 J_{-(l-\frac{1}{2})}] = 0 \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4.24)$$

Using

$$T_{r\theta} = \frac{2}{g}\left[\frac{1}{r}\frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{r} + \frac{\partial u_\theta}{\partial r}\right]$$

$$\hat{T}_{r\theta} = \frac{2\Upsilon}{g}\left[\frac{1}{r}\frac{\partial \hat{u}_r}{\partial \theta} - \frac{\hat{u}_\theta}{r} + \frac{\partial \hat{u}_\theta}{\partial r}\right]$$

it can be shown that $\hat{T}_{r\theta} = T_{r\theta}$ at $r = 1+\epsilon_1 P_2$ gives

$$A[2(l^2-1)\{1+(l-2)\epsilon_1 P_2\}]+C[2(l^2-1)J_{l+\frac{1}{2}}-\hat{h}^2 J_{l+\frac{1}{2}} +2\hat{h} J_{l+3/2}+\epsilon_1 P_2\{2(l^2-1)(l-2)J_{l+\frac{1}{2}} -2(l^2+l+2)\hat{h} J_{l+3/2}-(l-2)\hat{h}^2 J_{l+\frac{1}{2}}+\hat{h}^3 J_{l+3/2}\}] -\frac{B}{k}2l(l+2)\{1-\epsilon_1 P_2(l+3)\}-\frac{D}{k}[2l(l+2)J_{-(l+\frac{1}{2})} +2hJ_{-(l-\frac{1}{2})}-h^2 J_{-(l+\frac{1}{2})}-\epsilon_1 P_2\{2l(l+2)(l+3)J_{-(l+\frac{1}{2})} +2(l^2+l+2)hJ_{-(l-\frac{1}{2})}-(l+3)h^2 J_{-(l+\frac{1}{2})} -h^3 J_{-(l-\frac{1}{2})}\}] = 0 \quad \ldots \quad \ldots \quad \ldots \quad \ldots(4.25)$$

Finally the condition

$$\hat{T}_{rr} = T_{rr} - \frac{2}{We}\left(\frac{1}{\chi_1}+\frac{1}{\chi_2}\right) \text{ at } r = 1+\epsilon_1 P_2$$

will have to be used

$$\frac{1}{\chi_1}+\frac{1}{\chi_2} = \frac{2}{r}-\frac{2\zeta}{r^2}-\frac{1}{r^2}\left[\frac{1}{\sin^2\theta}\frac{\partial^2 \zeta}{\partial \phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \zeta}{\partial \theta}\right)\right]$$

for $r = 1+\zeta(\theta, \phi)$ (Landau and Lifshitz[51]).

For $r = 1+\epsilon_1 P_2+\epsilon P_l e^{it}$,

$$\frac{1}{\chi_1}+\frac{1}{\chi_2} = 2+4\epsilon_1 P_2+(l-1)(l+2)\epsilon P_l e^{it}$$

ϵ can be eliminated by using

$$\int_0^t \hat{u}_r dt = 1+\epsilon_1 P_2+\epsilon P_l e^{it}$$

Then after lengthy simplifications one arrives at the result

$$\frac{2\Upsilon i A}{l}(1+l\epsilon_1 P_2)+\frac{4\Upsilon A}{\hat{g}}(l-1)[1+(l-2)\epsilon_1 P_2] +\frac{4\Upsilon C}{\hat{g}}[(l-1)J_{l+\frac{1}{2}}-\hat{h} J_{l+3/2}+\epsilon_1 P_2\{(l-1)(l-2)J_{l+\frac{1}{2}} -\hat{h}^2 J_{l+\frac{1}{2}}+4\hat{h} J_{l+3/2}\}]-\frac{(l-1)(l+2)}{We}2i[A+CJ_{l+\frac{1}{2}} +\epsilon_1 P_2\{A(l-1)+C(l-1)J_{l+\frac{1}{2}}-C\hat{h} J_{l+3/2}\}] +\frac{2iB}{l+1}[1-(l+1)\epsilon_1 P_2]+\frac{4B(l+2)}{g}\{1-(l+3)\epsilon_1 P_2\} +\frac{4D}{g}[(l+2)J_{-(l+\frac{1}{2})}+hJ_{-(l-\frac{1}{2})}+\epsilon_1 P_2 \times\{-(l+2)(l+3)J_{-(l+\frac{1}{2})}-4hJ_{-(l-\frac{1}{2})} +h^2 J_{-(l+\frac{1}{2})}\}]=0 \quad \ldots \quad \ldots \quad \ldots(4.26)$$

Hence, the four boundary conditions represented by Eqs. (4.23)-(4.26), which are in the form of four homogeneous equations in A, B, C and D, can be made to satisfy simultaneously by making their secular determinant vanish. We shall restrict the present calculations to the case $l = 2$ (to save much of labour) and write the final characteristic equation in the form

$$\begin{vmatrix} -\hat{h}Q_{5/2}+\epsilon_1 P_2(-\hat{h}^2-15-\hat{h}Q_{5/2}^2+2\hat{h}Q_{5/2}) & 5 & \\ -\frac{\hat{h}^2}{2}+\hat{h}Q_{5/2}+\epsilon_1 P_2\left(-\frac{\hat{h}^2}{2}-6\hat{h}Q_{5/2}+\hat{h}^2 Q_{5/2}^2\right) & (1-\epsilon_1 P_2)\left(3-\frac{8}{k}\right) & \\ \Upsilon\hat{h}^2-4k\hat{h}Q_{5/2}-4k\epsilon_1 P_2\left(\hat{h}^2-\frac{\Upsilon h^2}{2k}+\hat{h}^2 Q_{5/2}^2\right) & \left[-2\hat{h}^2\left(\frac{\Upsilon}{2}+\frac{1}{3}\right)+4(k+4)+\frac{8\Upsilon h^2}{We}\right. & \\ & \left.+\epsilon_1 P_2\left\{-4h^2\left(\frac{\Upsilon}{2}+\frac{1}{3}\right)-4(k+4)\right\}\right] & \\ & hQ_{-\frac{1}{2}}+\epsilon_1 P_2(h^2+5hQ_{-\frac{1}{2}}+h^2 Q_{-\frac{1}{2}}^2) & \\ & \frac{h^2}{2k}-\frac{hQ_{-\frac{1}{2}}}{k}-\frac{\epsilon_1 P_2}{k}\left(\frac{h^2}{2}+4hQ_{-\frac{1}{2}}+h^2 Q_{-\frac{1}{2}}^2\right) & =0 \\ & \frac{2h^2}{3}+4hQ_{-\frac{1}{2}}+\epsilon_1 P_2\left(h^2+\frac{4h^2}{3}+16hQ_{-\frac{1}{2}}+4h^2 Q_{-\frac{1}{2}}^2\right) & \end{vmatrix}$$

$\ldots(4.27)$

As in the previous analyses, this can be simplified in the various limiting cases.

When $\Upsilon \to \infty$, $k \to \infty$, the determinantal equation (4.27) reduces to

$$[1+\epsilon_1 P_2-(2/\hat{h}^2)(1-\epsilon_1 P_2)-\sigma_{01}^2][\hat{h}^3(1+\epsilon_1 P_2) - 2\hat{h}^2 Q_{5/2}(1+3\epsilon_1 P_2)+\hat{h}^2\epsilon_1 P_2(\hat{h}+18)] = 3(1-\epsilon_1 P_2)[2\hat{h}(1-3\epsilon_1 P_2)-8Q_{5/2}-8\hat{h}Q_{5/2}^2\epsilon_1 P_2) \quad \ldots(4.28)$$

For $\epsilon_1 = 0$, i.e. a spherical drop, this is the same as Eq. (3.24), i.e. the result of Reid and Chandrasekhar. The contribution from deformation obviously occurs as a correction term.

Similarly, when $\Upsilon \to 0$, $k \to 0$,

$$[-\sigma_{02}^2+1+\epsilon_1 P_2-(24/h^2)(1-\epsilon_1 P_2)][2hQ_{-\frac{1}{2}}-h^2 + \epsilon_1 P_2\{24hQ_{-\frac{1}{2}}+2h^2Q_{-\frac{1}{2}}^2-2h^3Q_{-\frac{1}{2}}-h^2\}] = -8(1-\epsilon_1 P_2)[(12/h)Q_{-\frac{1}{2}}+2+\epsilon_1 P_2 \times\{4+(48/h)Q_{-\frac{1}{2}}+12Q_{-\frac{1}{2}}^2\}] \quad \ldots \quad \ldots \quad \ldots(4.29)$$

It agrees with the previous result for $\epsilon_1 = 0$, viz. Eq. (3.26). When the two phases have about the same density and viscosity, i.e. $\Upsilon = 1$, $k = 1$,

$$\sigma_{03}^2 = 1-\frac{5}{h(Q_{5/2}-Q_{-3/2})}+\epsilon_1 P_2+O\left(\frac{1}{h^2}\right) \quad \ldots(4.30)$$

In all the above equations, σ_{01}, σ_{02}, σ_{03} have the same meanings as in the section 'Oscillations of a Stationary Liquid Drop of Spherical Shape'. From all the above three equations, it is evident that the deviation of the drop from the spherical shape introduces a correction term of the order of the deviation in the expression for the frequency. Some of the numerical results obtained by taking into account the deviation from the spherical shape are given in Table 3.

Conclusion

In this paper we have attempted to discuss the oscillations of a liquid drop (or a gas bubble) relatively at rest in another fluid medium. Several physical factors like the viscosities, the inertial effects, the shape of the drop, the interfacial tension, etc., are found to contribute in nearly equal measures to the oscillation and it is not proper to neglect any one of them. The main results are as follows.

The deformation of the drop affects the oscillations. This is studied by taking the shape of the drop to be an oblate spheroid. In the simple case equivalent to Lamb's (where viscous effects are neglected), the expression becomes $\sigma^2 = \sigma_L^2[1-(\epsilon_1/4)]$, where σ_L is Lamb's frequency and ϵ_1, a measure of the deformation. The oscillations of highly deformed drops, as reported by Schoessaw and Boumeister, can easily be explained with this equation. The contribution from viscous terms has also been included and the correction terms to the frequencies are evaluated, but the main features remain unaltered.

The presence of viscosities of the media splits the frequencies into two modes — one lower and the other higher than Lamb's. The two frequency modes merge with Lamb's for the asymptotic cases when one of the phases has vanishing density and viscosity. For the phases of comparable density and viscosity and for drops of practical sizes, the deviation from Lamb's result is found to be considerable. From energy considerations, it follows that the lower frequency mode tends to appear in experimental observations. A preliminary comparison between the experimental results and the calculated values shows qualitative agreement, namely the observed frequencies are lower than Lamb's frequencies by 10-15%. The higher frequency mode has an indirect justification from the experimental results of Valentine *et al.* In order to reduce the interfacial tension of a drop A, small drops of B were made to coalesce with A and the oscillations were studied before and after coalescence. After coalescence the drop A was found to execute oscillations with a frequency larger than Lamb's by at least 30-40%. This can probably be explained with the help of the present calculations as follows. The small drop B had a large natural frequency which nearly matched with the higher mode frequency of A and thus inducing A to execute oscillations with that frequency.

For drops of sizes smaller than a critical size of the order of $\hat{\rho}\hat{\nu}^2/T$, the disturbances are damped aperiodically. Hence no oscillations for such small drops are possible. This critical size is very small ($\sim 10^{-4}$ cm) for a system like water-in-air, but assumes as large values as a few millimetres for drops in very viscous liquids.

A more critical examination of the theory shows that inertial effects present in the terminal motion of the drop may also give effects which are comparable to the deviations from Lamb's calculations, discussed here. Therefore, it appears premature to make a detailed discussion of the experimental results until this effect has been included in the theoretical calculations. Further theoretical work on this aspect of the problem and a complete discussion of the experimental results will be reported separately[62].

Summary

The oscillations of a liquid drop (or a gas bubble) relatively at rest in another fluid medium have been studied. The different types of oscillation of the drops and the factors that can cause their growth and decay are first briefly reviewed. The various factors, such as the viscosities, interfacial tension, inertial effects, the deformation of the drop, etc., give nearly comparable effects on the oscillations. The prolate-oblate oscillations of a spherical drop are then studied starting from the basic hydrodynamic equations, suitably reduced to non-dimensional form. For drops of sizes smaller than a certain critical size, which depends on the number $\hat{\rho}\hat{\nu}^2/T$, the disturbance of the surface is damped aperiodically without executing any oscillations at all. Similar behaviour is found to occur for all types of liquid-liquid systems, but this critical size attains practical importance for drops in very viscous liquids with low interfacial tension. Damped oscillations can occur in drops larger than this critical size. Two

possible oscillatory damping modes are found to exist, one with frequency lower and the other higher than Lamb's frequency. Though this deviation is small in the asymptotic cases of a drop oscillating in free space or a bubble in a dense viscous liquid, it becomes prominent (of the order of 10-20%) in the case of oscillations of a drop in a similar fluid. The lower frequency mode is the one that is observed in practice, whereas in some special circumstances, the higher mode can also be observed. The effect of deformation on the frequency of oscillation is studied by considering the initial drop shape to be an oblate spheroid. It is shown that Lamb's equation for a spherical drop gets modified and the resulting equation explains satisfactorily the experimental results on deformed drops. The effect of viscosities on the oscillations of these initially deformed drops is also evaluated. The calculations explain qualitatively the experimentally observed deviations from Lamb's frequencies, but a quantitative comparison can be made only after the effect of a steady terminal velocity of the drop on its oscillations is included.

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Nomenclature

$P_l(\xi)$ = perturbation of the drop surface expressed in Legendre polynomials of lth order with argument $\xi = \cos\theta$

T = interfacial tension between the drop phase and the external phase

U = terminal velocity of the drop in the outside medium

a, d = equilibrium radius (diam.) of the drop

r, θ, ϕ = coordinates of any point from the centre of the drop

f = vortex discharge frequency behind the drop

g, h = oscillation parameters defined by $h^2 = -ig = -i\sigma a^2/\nu$

δp = pressure change consequent on the perturbation

$T_{rr}, T_{r\theta}$ = radial and tangential stresses on the interface

U_r, U_θ = velocity components of the fluid

α, β = parameters depending on the frequency and damping of the oscillations

$\epsilon = \epsilon_0 e^{i\sigma t}$ = perturbation of the interface

ϵ_1 = defines the deformation of the drop from Eq. (4.1)

ν = kinematic viscosity of the medium

ρ = density of the fluid medium

$\sigma = \sigma_r + i\sigma_i$ = generalized oscillation frequency representing both the oscillation and the damping parts

$\sigma_{01}, \sigma_{02}, \sigma_{03}, \sigma_L$ = Lamb's oscillation frequencies in various limiting cases

χ_1, χ_2 = principal radii of curvature at the drop surface

$\Psi, \Delta\Psi$ = stream function and its perturbation

$Re = Ua/\nu$ = Reynolds' No.

$We = \rho a U^2/T$ = Weber No. (A characteristic 'Weber number' $\rho a^3\sigma^2/T$ is also introduced for a stationary drop with $U = 0$)

$Sr = fd/U$ = Strouhal No.

$\gamma = \hat{\rho}/\rho$ = ratio of the density of the drop to the external phase

$k = \hat{\mu}/\mu = \gamma(\hat{\nu}/\nu)$ = ratio of the viscosities of the drop and the outside medium

$\rho\nu^2/T$, $\sigma_L a^2/\nu$ = dimensionless numbers determining the critical size of the drop for oscillations to start

$\hat{}$ = drop phase parameter (labelled by a carat sign)

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APPENDIX 1

Evaluation of $Q_{5/2}(h)$ and $Q_{-3/2}(h)$ in Terms of α and β

Since $h^2 = -i\sigma a^2/\nu = \alpha^2(\beta - i)$ where $\alpha^2 = \sigma_r a^2/\nu$, $\beta = \sigma_i/\sigma_r$

$$h = \alpha\left[\frac{1}{\sqrt{2}}\left\{\beta \pm (\beta^2+1)^{\frac{1}{2}}\right\}^{\frac{1}{2}} - \frac{i}{\sqrt{2}}\left\{\beta \pm (\beta^2+1)^{\frac{1}{2}}\right\}^{-\frac{1}{2}}\right]$$

$$= \frac{\alpha}{\sqrt{2}}\left[(1+\tfrac{1}{2}\beta) - i(1-\tfrac{1}{2}\beta)\right] \quad \text{for } \alpha > 0(10),\ \beta < 0(1)$$

$$= x + iy \text{ say}$$

The expressions for Bessel functions of half-integral orders with complex arguments can be written as follows:

$$\text{(a)}\ \sqrt{\frac{\pi x}{2}}\,J_{5/2}(x) = \left(\frac{3}{x^2} - 1\right)\sin x - \frac{3}{x}\cos x$$

changing x to $(x+iy)$ and using the approximations $\cosh y = \sinh y$ for $y \gg 10$; the expression for $J_{5/2}(x-iy)$ can be simplified to the form

$$\left[\frac{\pi}{2}(x-iy)\right]^{\frac{1}{2}} J_{5/2}(x-iy) \simeq ie^{ix}\sinh y\left[1 - \frac{3(1-\frac{1}{2}\beta)}{\sqrt{2}\alpha}\right]$$

Similarly, it can be shown that

$$\left[\frac{\pi}{2}(x-iy)\right]^{\frac{1}{2}} J_{7/2}(x-iy) \simeq e^{ix}\sinh y\left[1 - \frac{6(1-\frac{1}{2}\beta)}{\sqrt{2}\alpha} + \frac{6i(1+\frac{1}{2}\beta)}{\sqrt{2}\alpha}\right]$$

Hence, one can write

$$Q_{5/2}(x-iy) \simeq \frac{6(1+\frac{1}{2}\beta)+6i(1-\frac{1}{2}\beta)-i\sqrt{2}\alpha}{\sqrt{2}\alpha - 3(1-\frac{1}{2}\beta)}$$

(b) Again using the expressions for $J_{-3/2}(x)$ and $J_{-5/2}(x)$

$$\sqrt{\frac{\pi x}{2}}\,J_{-3/2}(x) = -\sin x - \frac{\cos x}{x}$$

$$\sqrt{\frac{\pi x}{2}}\,J_{-5/2}(x) = \frac{3\sin x}{x} + \left(\frac{3}{x^2} - 1\right)\cos x$$

it can be shown that

$$\left[\frac{\pi}{2}(x-iy)\right]^{\frac{1}{2}} J_{-3/2}(x-iy) = e^{ix}\sinh y\left[i - \frac{i(1-\frac{1}{2}\beta)}{\sqrt{2}\alpha} - \frac{1+\frac{1}{2}\beta}{\sqrt{2}\alpha}\right]$$

and

$$\left[\frac{\pi}{2}(x-iy)\right]^{\frac{1}{2}} J_{-5/2}(x-iy) = -e^{ix}\sinh y\left[1 - \frac{3(1-\frac{1}{2}\beta)}{\sqrt{2}\alpha} + \frac{3i(1+\frac{1}{2}\beta)}{\sqrt{2}\alpha}\right]$$

and hence

$$Q_{-3/2}(x-iy) = \frac{-\sqrt{2}(1+\frac{1}{2}\beta) - i\alpha + 2\sqrt{2}i(1-\frac{1}{2}\beta)}{\alpha - 3\sqrt{2}(1-\frac{1}{2}\beta)}$$

These expressions for $Q_{5/2}(x-iy)$ and $Q_{-3/2}(x-iy)$ are valid for $y > 10$.

APPENDIX 2

Relation Between α and β to Satisfy the Characteristic Equation in Full

The characteristic equation (3.23) of a drop oscillating in a liquid medium or the asymptotic equations (3.24, 3.26, 3.27) are all complex equations, since σ is a complex quantity. Also the two parameters α and β are closely related to the real and imaginary parts of σ. Hence, an approximate relation between them can be derived by separating the equations into its real and imaginary parts. We shall first consider the asymptotic cases.

(a) Relation between α and β for the case of a stationary spherical drop for ($\gamma \to \infty$, $k \to \infty$, $l = 2$); Eq. (3.24) can be recast in the form

$$-\frac{\sigma_L^2}{\sigma_r^2} = (1+2i\beta)\left[\frac{4}{\hat{h}^2} - 1 + \frac{6(1-4Q_{5/2}/\hat{h})}{\hat{h}^2 - 2\hat{h}Q_{5/2}}\right] \qquad \text{...(A.1)}$$

where

$$\hat{h}^2 = \alpha^2(\beta - i) = -i\sigma a^2/\hat{\nu}$$

$$\hat{h} = \alpha/\sqrt{2}\,[(1+\tfrac{1}{2}\beta) - i(1-\tfrac{1}{2}\beta)] = x + iy$$

$$Q_{5/2} = Q_r + iQ_i = \frac{6(1+\beta)+6i-i\sqrt{2}\alpha(1+\frac{1}{2}\beta)}{\sqrt{2}\alpha(1+\frac{1}{2}\beta)-3} \qquad \text{...(A.2)}$$

Simplification can be carried out by neglecting terms of the order α^2, $1/\beta^2$, etc.

$$\frac{1}{\hat{h}^2 - 2\hat{h}Q_{5/2}} \simeq \frac{1}{\alpha^2}\left[i + \frac{2\alpha\beta + 2\sqrt{2}i}{2\alpha\beta + 2\alpha - 10\sqrt{2}}\right]$$

$$1 - \frac{4Q_{5/2}}{\hat{h}} \simeq 1 - \frac{4(1-i-i\beta+12i/\sqrt{2}\alpha}{\sqrt{2}\alpha(1+\frac{1}{2}\beta)-3}$$

Hence

$$-\frac{\sigma_L^2}{\sigma_r^2}=(1+2i\beta)\left[\frac{6}{\alpha^2}\left\{i+\frac{2\alpha\beta+2\sqrt{2}i}{2\alpha\beta+2\alpha-10\sqrt{2}}\right\}\times\left\{1-\frac{4(1-i-i\beta+12i/\sqrt{2}\alpha)}{\sqrt{2}\alpha(1+\frac{1}{2}\beta)-3}\right\}-1+4i/\alpha^2\right]$$

The imaginary part of the right-hand side of the above equation can be equated to zero, thus giving

$$\beta=5/\alpha^2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.3)$$

Also for the other case when $Q_{5/2}$ is negative, one gets

$$\beta'=5/\alpha^2 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.3')$$

(b) Relation between α and β for the case of a stationary spherical drop for $\gamma\to 0$, $k\to 0$, $l=2$. The characteristic Eq. (3.26) is written in the form

$$-\frac{\sigma_L^2}{\sigma_r^2}=(1+2i\beta)\left[-1+\frac{24}{h^2}+\frac{16(1+6Q_{-3/2}/h)}{h^2-2hQ_{-3/2}}\right] \quad \ldots(A.4)$$

Making use of Eq. (A.2) and

$$Q_{-3/2}=\frac{-\sqrt{2}(1+\frac{1}{2}\beta)-i\alpha+2\sqrt{2}i(1-\frac{1}{2}\beta)}{\alpha-3\sqrt{2}(1-\frac{1}{2}\beta)} \quad \ldots(A.5)$$

one can show with the similar approximations that

$$h^2-2hQ_{-3/2}\simeq\alpha^2\beta-3\sqrt{2}\alpha\beta-2-i\alpha^2+5\sqrt{2}i\alpha-\frac{3}{\sqrt{2}}i\alpha\beta-6i$$

$$\frac{1}{h^2-2hQ_{-3/2}}\simeq\frac{1}{\alpha^2}\frac{\alpha\beta+i\alpha-5\sqrt{2}i}{\alpha-10\sqrt{2}}$$

$$\frac{Q_{-3/2}}{h}\simeq\frac{\alpha(1-\frac{1}{2}\beta)-3\sqrt{2}+\sqrt{2}i-i\alpha(1+\frac{1}{2}\beta)}{\alpha(\sqrt{2}\alpha-6)}$$

Imaginary part of

$$(1+2i\beta)\left[-1+\frac{24(\beta+i)}{\alpha^2}+\frac{16}{\alpha^2}\frac{\alpha\beta+i\alpha-5\sqrt{2}i}{\alpha-10\sqrt{2}}+O\left(\frac{1}{\alpha^3}\right)\right]$$

equated to zero gives

$$\beta\simeq\frac{20}{\alpha^2}\left(\frac{\alpha-8\sqrt{2}}{\alpha-10\sqrt{2}}\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.6)$$

For other equally probable case of $Q_{-3/2}$ negative, we similarly get

$$\beta'\simeq\frac{4}{\alpha^2}\left(\frac{5\alpha-8\sqrt{2}}{\sigma-2\sqrt{2}}\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.6')$$

(c) Relation between α and β for the case of a stationary spherical drop for $\Upsilon=1$, $k=1$, $l=2$. Here we have the relation (3.27);

$$\frac{\sigma_L^2}{\sigma_r^2}=(1+2i\beta)\left[1-\frac{5}{2h(Q_{5/2}-Q_{-3/2})}\right] \quad \ldots \quad \ldots(A.7)$$

One can easily show, using Eqs. (A.2) and (A.5), that

$$Q_{5/2}-Q_{-3/2}\simeq\frac{8(1+\beta)+5i}{\sqrt{2}\alpha(1+\frac{1}{2}\beta)-9} \quad \ldots \quad \ldots(A.8)$$

and hence imaginary part of σ_L^2/σ_r^2 is equal to

$$2\beta-\frac{5\sqrt{2}}{\alpha}\frac{(55\beta+6)(\sqrt{2}\alpha-9)}{712+1024\beta}$$

which on equating to zero gives

$$\beta\simeq\frac{2\alpha-9\sqrt{2}}{4{\cdot}4\alpha+82{\cdot}5\sqrt{2}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.9)$$

Similarly, taking the other possibility of $Q_{5/2}$ positive and $Q_{-3/2}$ negative, we get

$$Q_{5/2}+Q_{-3/2}\simeq\frac{4-2\sqrt{2}i\alpha+19i}{\sqrt{2}\alpha-9}$$

and hence, one can show that

$$\beta'=\frac{10}{32\alpha}\frac{2\sqrt{2}\alpha-33}{\alpha-9\sqrt{2}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots(A.10)$$

For the other two possibilities of $Q_{5/2}$ negative, $Q_{-3/2}$ positive and both negative, β'', β''' turn out to be negative for the useful range of α. Hence, they are physically invalid solutions.

For the general case of the oscillations of a liquid drop in a liquid medium, the full equation (3.22) is utilized and numerical simplification is carried out to find β for given α.

The numerical values of β for various values of α have been calculated in all the above cases and are given in Tables 1-4.

Application of the Aldehyde-Nitroalkane Procedure to Carbohydrate Chemistry

H. G. GARG

Department of Chemistry, University of Roorkee, Roorkee

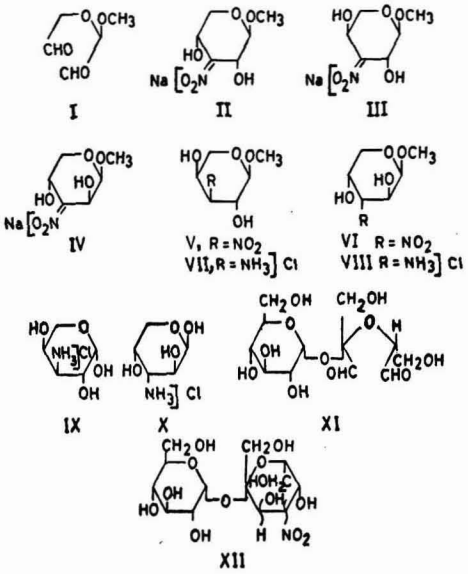
THE well-known base-catalysed condensation of an aldehyde with nitroalkanes and in particular nitromethane[1], a reaction analogous to the aldol condensation, was first applied to the field of carbohydrate chemistry by Sowden and Fischer[2]. Interest in the synthesis of nitro sugars via the Fischer nitroalkane cyclization[3,4] (periodate cleavage of a sugar derivative and subsequent cyclization with nitroalkane) is derived from two considerations. First, they would presumably be capable of reduction and thereby serve to complement the existing methods of synthesizing different series of amino sugars, viz. furanosides, pyranosides, septanoside, etc., of which some members, notably puromycin[5,6] and kanamycins[7-9], have drawn considerable biochemical and medicinal attention. Secondly, certain analogues might exhibit physiological activity. Ring closure by nitroalkane addition leads to 3-deoxy-3-nitro-aldo-[10,11] or departing from ketosides to 4-deoxy-4-nitroketopyranosides[12-14]. The reaction sequence can result in a chain prolongation (e.g. conversion of a furanoside to pyranoside) or conversely shortening (e.g. conversion of a pyranoside to furanoside) 'from within'. The rapid progress in this field provided the stimulus for writing this review.

3-Amino-3-Deoxypyranoses

L'-Methoxyglycolic aldehyde (I)[15,16] on cyclization with nitromethane and sodium methoxide in aqueous alcohol leads to a mixture of isomeric salts of β-D-*erythro* (II), α-L-*threo* (III), and β-D-*threo* (IV) of methyl 3-deoxy-3-*aci*-nitropentopyranoside sodium[17]. Compounds III and IV occur as minor components besides the chief product II. Although compounds III and IV could not be isolated as such, their presence was indicated[18] by the isolation of two new, free nitroglycosides (V) and (VI) by deionization of the mixture; methyl 3-deoxy-3-nitro-α-L-arabinopyranoside (V) from III, and methyl 3-deoxy-3-nitro-β-D-arabinopyranoside (VI), arising from IV were obtained in 5% yield respectively. These crystalline nitroglycosides were hydrogenated to furnish the corresponding aminoglycosides (VII) and (VIII), which crystallized as hydrochlorides. Proof of the structure and configuration of VII and VIII was afforded by acid hydrolysis yielding 3-amino-3-deoxy-β-L-arabinose hydrochloride (IX) and 3-amino-3-deoxy-β-D-arabinose hydrochloride (X). The physical constants of the new nitro and amino sugar derivatives obtained using similar sequences are given in Table 1.

4-Amino-4-Deoxypyranoses

Ring closures of dialdehydes from ketosides lead to 4-deoxy-4-nitroketopyranosides. The 4-deoxy-4-nitro-(or amino)-ketopyranosides from monosaccharides are summarized in Table 2.



The dialdehyde (XI) that arises from a partial $Pb(OAc)_4$ cleavage of sucrose on cyclization with nitromethane yields a streoisomeric mixture of nitrodisaccharide (XII). Upon catalytic hydrogenation, a single amino disaccharide, α-D-glucopyranosyl-4-amino-4-deoxy-β-D-glucoheptulopyranoside hydrochloride is obtained[13].

3-Amino-3-Deoxyheptose

Condensation of the dialdehyde (XIV) from methyl 4,6-O-ethylidene-α-D-glucoside (XIII) by periodate oxidation with $CH_3NO_2/NaOCH_3$ and subsequent acidification with a cation exchange resin gave methyl 3-deoxy-3-nitro-5,7-O-ethylidene-D-*glycero*-α-D-mannoseptanoside (XV), m.p. 183-6°; $[\alpha]_D$ 41·7° (pyridine) in 41% yield. Catalytic hydrogenation, followed by acid hydrolysis, affords a syrupy 3-amino-3-deoxy-D-*glycero*-D-mannoheptopyranose (XVI) which can, however, be crystallized as its

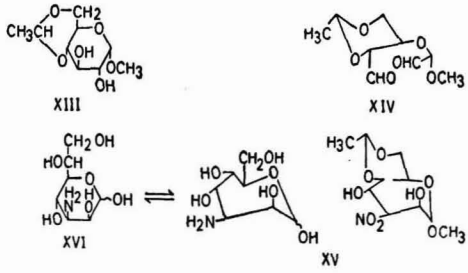


TABLE 1 — PHYSICAL DATA OF THE NEW NITRO AND AMINO SUGAR DERIVATIVES

(Unless otherwise stated, all rotations are in water)

Dialdehyde used	Configuration	3-Deoxy-3-nitro-		3-Amino-3-deoxy-		Ref.
		m.p. °C	$[\alpha]_D$	m.p. °C	$[\alpha]_D$	
L′-Methoxydiglycolic aldehyde	Methyl α-L-arabinopyranoside	180-82	+85·5	HCl, 164-5 (d)	+24·7	17
	Methyl β-D-arabinopyranoside	178-9·5	−278	HCl, 181-3 (d)	−205	—
D′-Methoxydiglycolic aldehyde	Methyl α-D-arabinopyranoside	179-80	−86	165	−24·7	17
	Methyl β-L-arabinopyranoside	179-80	+278	180-83	+202	
L′-Methoxy-D-hydroxymethyl-diglycolic aldehyde	Methyl β-D-glucopyranoside	204-5	−12	207-8 (d)	−34	19, 20
	Methyl β-D-galactopyranoside	—	—	—	—	—
	Methyl β-D-mannopyranoside	—	—	—	—	—
D′-Methoxy-D-hydroxymethyl-diglycolic aldehyde	Methyl α-D-glucopyranoside	—	—	—	—	—
	Methyl α-D-mannopyranoside	—	—	HCl, 205 (d)	+62·8	21-23
	Methyl α-D-talopyranoside	—	—	—	—	—
L′-Methoxy-L-methyldiglycolic aldehyde	Methyl-6-deoxy-α-L-glucopyranoside	—	—	177-8	−145	24, 25
D′-Methoxy-D-methyldiglycolic aldehyde	Methyl 6-deoxy-α-D-glucopyranoside	—	—	175-7	+148	26, 27
cis-1,3-Dioxolan-2,4-dicarboxaldehyde[28]	1,6-Anhydro-β-D-gulopyranose	163-4	+84	HCl, 229-30 (d)	+46	29, 30
	1,6-Anhydro-β-D-idopyranose	—	—	193-6 (d)	−93	—
	1,6-Anhydro-β-D-altropyranose	—	—	HCl, 214 (d)	−170	—
D′-Methoxy-D-hydroxymethyl-diglycolic aldehyde	Methyl 3-deoxy-3-C-methyl-β-L-*gluco* (or *allo*)-pyranoside	—	—	235-7	+40·5	31
	Methyl 3-deoxy-3-C-methyl-α-D-*gluco* (or *allo*)-pyranoside	—	—	186-8	+135	—
L′-Methoxy-D-hydroxymethyl-diglycolic aldehyde	Methyl 3-deoxy-3-C-methyl-β-D-*gluco* (or *allo*) pyranoside	—	—	235-7	−40·9	31
	Methyl 3-deoxy-3-C-methyl-α-L-*gluco* (or *allo*)-pyranoside	—	—	185-7	−134·2	—
cis-1,3-Dioxolan-2,4-dicarboxaldehyde	2,4-Dideoxy-β-D-idoson	2,4-di-(benzylamino), 121-3	−73·5 ($CHCl_3$)	2,4-Diamino trihydrochloride, 189-90 (d)	−48·3	32

TABLE 2 — PHYSICAL DATA FOR 4-DEOXY-4-NITRO- (OR AMINO)-KETOPYRANOSIDES

(Unless otherwise stated, all rotations are in water)

Dialdehyde used	Configuration	4-Deoxy-4-nitro-		4-Amino-4-deoxy-		Ref.
		m.p. °C	$[\alpha]_D$	m.p. °C	$[\alpha]_D$	
2-Hydroxy-*cis*-1,3-dioxolan-2,4-dicarboxaldehyde	2,7-Anhydro-β-D-alloheptulopyranose	176	−60	—	−55	12, 33
	2,7-Anhydro-β-D-altroheptulopyranose	159	−176·5	—	−126	—
	2,7-Anhydro-β-D-guloheptulopyranose	203	+69	—	+39·0	—
L′-Benzyl-D-hydroxymethyl-diglycolaldehyde	Benzyl α-L-sorbopyranoside	131	−61·2 (MeOH)	—	—	14
	Benzyl β-D-tagatopyranoside	—	—	—	—	—

N-acetate, m.p. 103-5°; $[\alpha]_D$ +2·8° (2·5 min)→ −10·9° (4 hr)[34].

Aminopolyols

The cyclization of polysaccharide dialdehyde obtained by the oxidation of cellulose with nitromethane and sodium hydroxide in aqueous solution gives products which contained 2·4-5·0% nitrogen, depending on the concentration of alkali (0·32-1·44%) and the reaction time (20-48 hr) at room temperature (Chart 1)[35].

The structures of these products have not been defined unequivocally. It was assumed that the major product contained a seven-membered ring, together with other products.

Starch[36], xylanes, alginic acids (Hanessian's unpublished work) and polygalacturonic acids (Hanessian's unpublished work), dialdehydes with nitro-

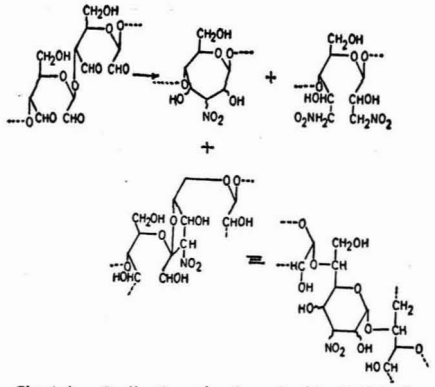


Chart 1 — Cyclization of polysaccharide dialdehyde

methane cyclization yield pale yellow solid products (nitropolyol) containing about 2-4% N. Catalytic hydrogenation leads to aminopolyols.

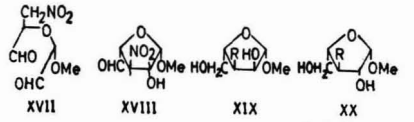
3'-Amino-3'-Deoxynucleosides

The synthesis of 3'-amino-3'-deoxyhexopyranosyl nucleosides by treatment of nucleoside dialdehyde with nitromethane followed by reduction of the nitro group has been achieved by two independent groups[37-45].

Thus, the dialdehydes from uridine[46], 3-(β-D-glucopyranosyl)thymine[47], adenosine, 6-dimethyl-amino-9-β-(D-ribofuranosyl)purine[48,49], inosine and 7-(β-D-glucopyranosyl)theophylline[50] obtained by periodate oxidation lead to a mixture of 3-deoxy-3-nitrohexopyranosyl nucleosides. The latter on reduction yields 3-amino-3-deoxyhexopyranosyl derivatives (Table 3).

3-Amino-3-Deoxyfuranoses

Periodic acid oxidation of methyl 6-deoxy-6-nitro-α-D-glucopyranoside to dialdehyde (XVII) and internal nitromethane addition in the latter at *p*H 7·5 leads to a mixture of streoisomeric methyl 5-*aldo*-3-deoxy-3-nitro-pentofuranosides (XVIII) and subsequent sodium borohydride reduction gives crystalline methyl 3-deoxy-3-nitro-β-L-ribofuranoside (XIX, major isomer) and methyl 3-deoxy-3-nitro-β-L-arabinofuranoside (XX, minor isomer). Catalytic hydrogenation leads to corresponding amine hydrochloride[53].



XVII XVIII XIX XX

R = NO_2 or NH_2

Stereochemical Considerations

The nitroalkane condensations do not appear to proceed in a streospecific way, although a notable streochemistry is always observed. The two asymmetric centres derived from C-1 and C-5 of nitro (or amino) sugars of the dialdehyde are not involved in either the periodate scission or the nitroalkane condensation. The configurations at C-2 and C-4 in the main product are predictable from Cram's rule[34]. An *aci*-nitro-deoxy sugar is symmetrical at C-3 and there remain four configurations which the

TABLE 3 — PHYSICAL DATA FOR 3-DEOXY-3-NITRO- AND 3-AMINO-3-DEOXYHEXOPYRANOSYL NUCLEOSIDES

(Unless otherwise stated, all rotations are in water)

Dialdehyde obtained from	Configuration of the cyclized nucleosides	3-Deoxy-3-nitro-		3-Amino-3-deoxy-		Ref.
		m.p. °C	$[\alpha]_D$	m.p. °C	$[\alpha]_D$	
Uridine	β-D-Glucopyranosyl-	H_2O, 162-4	+36	HCl, 180 (d)	20	31, 37
	β-D-Galactopyranosyl-	—	—	HCl, 234-5	+67	40, 42
	β-D-Mannopyranosyl-	—	—	—	—	—
3-(β-D-Glucopyranosyl)thymine	β-D-Glucopyranosyl-	170-75	+17 (MeOH)	155	+27 (MeOH)	43
Adenosine	β-D-Glucopyranosyl-	—	—	*	*	39
	β-D-Glactopyranosyl-	—	—	*	*	—
	β-D-Mannopyranosyl-	—	—	*	*	—
Inosine	β-D-Glucopyranosyl-	202-5 (d)	−4	HCl, 200	+2	42
7-(β-D-Glucopyranosyl)theophylline	β-D-Glucopyranosyl	160-62	+12 (DMSO)	—	—	44
	β-D-Mannopyranosyl-	224-6	+132 (DMSO)	207-9	+107	—
	β-D-Galactopyranosyl-	196-7 (d)	+13 (DMSO)	132-4	+38	—
Uridine (with nitroethane)	3-C-Methyl-D-glucopyranosyl-	226-40 (d)	+25·5	H_2O, 146-8	+39	51, 52
	3-C-Methyl-D-mannopyranosyl-	H_2O, 189-90	+121 (MeOH)	—	—	—
	3-C-Methyl-D-galacto-pyranosyl-	H_2O, 157-60	+50 (MeOH)	—	—	—

*Crystalline 9-(3-acetamido-3-deoxy-2,4,6-tri-O-acetyl-β-D-hexosyl)-adenines are obtained.

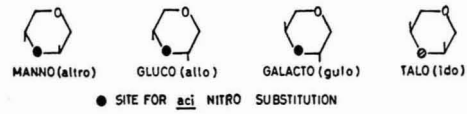


Chart 2 — Four possible configurations of 3-deoxy-3-*aci*-nitro derivatives

molecules may assume when they are being formed. These are *manno* (*altro*), *gluco* (*allo*), *alo* (*ido*) and *galacto* (*gulo*) configurations. The nitro group obtained by acidification of the *aci*-nitro salts preferentially assumes the equatorial position, i.e. the proton is attached from the axial side (Chart 2).

In several studies on the application of the periodate-nitroalkane procedure to glycosides[23] and nucleosides[37-44] only three isomers in different yields with *gluco*, *galacto* and *manno* configurations have been isolated. The yields of different isomers depend on the thermodynamic stabilities of the *aci*-nitro salts[17,23].

The cyclization products obtained from 1,3-dioxolan-2,4-dicarboxaldehyde and nitromethane (Table 1) have *gulo*, *ido* and *altro* configurations[29,30]. The rigidity of the dialdehyde due to the 1,6-anhydro bridge (vicinal to the aldehydo group) appears to have a much greater effect at C-2 and C-4.

Summary

Recent advances in the application of the aldehyde-nitroalkane procedure to carbohydrate chemistry are reviewed. The syntheses of 3-amino-3-deoxypyranoses, 4-amino-4-deoxyheptose, aminopolyals, 3'-amino-3'-deoxynucleosides and 3-amino-3-deoxyfuranoses and the stereochemistry of the amino sugars are discussed.

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Occurrence, Distribution & Properties of Lysosomes

V. NINJOOR, P. L. SAWANT & A. SREENIVASAN

Biochemistry & Food Technology Division, Bhabha Atomic Research Centre, Trombay, Bombay 85

THE study of the living cell in recent years has revealed an increasingly complete picture of its working parts and has enabled the identification of these parts with their functions. This has been possible through collaborative approaches from several biological disciplines. Especially significant are the contributions of the cell anatomist and the biochemist. The cell anatomist has carried out intensive studies of the cell in almost molecular detail with the help of the electron microscope. The biochemist, using the techniques of disruption and fractionation, has defined the cellular organelles and their minute components in isolation from one another. These studies have accomplished the task of understanding cell structure and function more or less completely.

This concurrent study of structure and function has shown that while the nuclei store and retrieve genetic information, the mitochondria conduct the primary energy transformations of the cell, ribosomes being the centres of enzyme synthesis. The recognition of the lysosome as a distinct organelle and its role in cellular economy has been comparatively more recent.

Occurrence and Distribution of Lysosomes

First identified in rat hepatic cells in 1955 by de Duve, lysosomes were found to occur in most mammalian cells, such as liver[1], spleen[2], kidney[3], brain[4], gut[5], thyroid gland[6], leucocytes[7], macrophages[8], pancreas[9], prostate[10], ovary[11], uterus[12], muscle[12], heart[13], synovium[14], skin[15], spinal ganglions[16], lymph nodes[17], lymphoid tissue[18] and bladder[19]. They have also been found in invertebrates[20] and in unicellular organisms[21]. Lysosomal activity has been shown to be present in plants[22] as well as in bacteria[23]. Tappel *et al.*[24] examined extensively the distribution of lysosomes in animal cells. All these studies indicated that lysosomes occur in many, possibly in all, animal cells.

Biochemical Definition and Main Properties of Lysosomes

Lysosomes are the cytoplasmic particles, presumably spherical in shape, with a mean diameter of 0·4 μ and an average density of 1·15 when suspended in 0·25*M* sucrose solution. They are supposed to possess a bag-like structure containing powerful digestive enzymes having an acid *p*H optimum. Lysosomal enzymes, like other proteins, are synthesized in ribosomes within the folded membranes of the endoplasmic reticulum[25].

The main properties of rat liver lysosomes, as revealed by their behaviour *in vitro*, are illustrated schematically in Fig. 1. The lipoprotein membrane acts as an effective barrier between the enzymes and their substrates, with the result that intact particles are practically inactive enzymically on external substrates. The various kinds of treatments listed in Fig. 1 all cause the membrane to

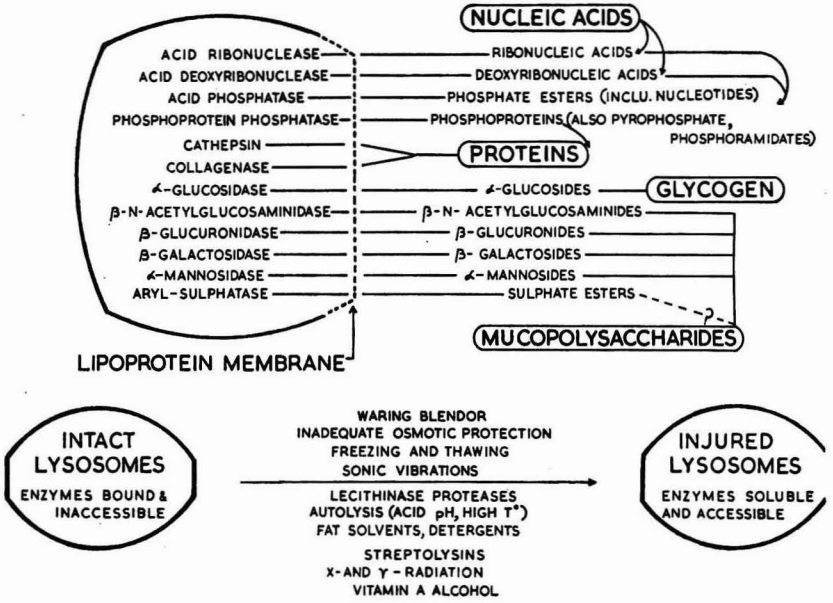

Fig. 1 — Schematic representation of lysosomal activities (modified from de Duve[28])

TABLE 1 — ENZYMES AND OTHER SUBSTANCES EXISTING IN LYSOSOMES*

ENZYMES

Acid phosphatase; acid ribonuclease; acid deoxyribonuclease; acid proteases; cathepsins; phosphoprotein phosphatase; β-glucuronidase; β-N-acetylglucosaminidase; α-mannosidase; β-galactosidase; α-glucosidase; hyaluronidase; lysozyme; phospholipase; acid lipase; phosphatidic acid phosphatase; collagenase; arylsulphatase A & B; nonspecific esterases

OTHER SUBSTANCES

Phagocytin; cationic 'inflammatory protein'; mucopolysaccharides; glycoproteins; plasminogen activator; permeability inducing protease; hemolysin (or hemolysins); unidentified basic proteins

*Based on the reports of Weissmann[78,104].

become injured by a variety of mechanisms, and consequently to bring about a partial or complete unmasking of the enzyme activities. This phenomenon is generally associated with the release of enzymic proteins into the soluble phase, but there may be limiting conditions where penetration of substrates becomes possible while the enzymes are still retained by the partially damaged membrane.

The enzymes and other substances existing in the lysosomes have been listed in Table 1.

Types of Lysosomes

Since lysosomes are known to participate in the intracellular digestion and engulfing processes, they exhibit different forms, depending on their function. The primary lysosome or the 'nascent granule' form of lysosome which is present in polymorphonuclear leucocytes and macrophages merges with the membranes of the endocytic (comprising both pinocytic and phagocytic) vacuoles or 'phagosomes'[26] resulting in a structure known as 'phagolysosome'[27] or digestive vacuole[28]. This phenomenon occurs when the cell takes up protein, microorganisms or inert particles[29], and gives rise to digestion of the ingested material.

Intracellular digestion may also take place when lysosomes ingest cellular materials like mitochondria, Golgi vesicles and endoplasmic reticulum, resulting in the formation of 'autophagic vacuole'.

Lysosomes either as phagosomes or as autophagic vacuoles, that have carried out digestive functions, finally appear filled with debris, usually of a lipid nature. These structures are termed as 'residual bodies'[28,30] and it is practically impossible to determine whether such bodies result by digestion of foreign matters (phagolysosomes) or by auto-digestion (autophagic vacuoles) or both. When residual bodies which have been shown to be capable of participating in further acts of endocytosis and digestion[31] amass several membranous arrays that resemble the ultrastructure of nervous tissue, the final forms are referred to as 'myelin fibres'[29,32]. Sometimes the components of Golgi apparatus unite together with the endocytic vesicles during intense pinocytic stimulation. The resultant organelles are known as 'multivesicular bodies'[25]. The various types of lysosomes present in the animal cell are represented in Fig. 2.

The Morphological Concept

Identification of lysosome with cytochemical techniques alone has been found difficult due to contamination with mitochondria and other subcellular organelles. So, it was always found necessary to interpret the results obtained by morphological studies with biochemical findings.

Acid phosphatase, one of the lysosomal enzymes, has been used as a marker enzyme in cytochemical and electron micrograph studies of lysosomes. Novikoff and his colleagues[33] examined the various fractions, collected by differential centrifugation of rat liver homogenate, with electron microscope. The fractions were found to contain mitochondria, microsomes, 'pericanalicular dense bodies'[34,35] and the micro-bodies[36]. Using Gomori technique[37] for the identification of acid phosphatase activity, and then fixing in the electron microscope, they succeeded in localizing maximum enzyme activity only in the dense bodies. Further cytochemical studies have shown that lysosomes are indistinguishable from pericanalicular dense bodies[38,39]. Microbodies containing urate oxidase, catalase and D-amino acid oxidase[40] have been proved to be a separate entity by density gradient centrifugation

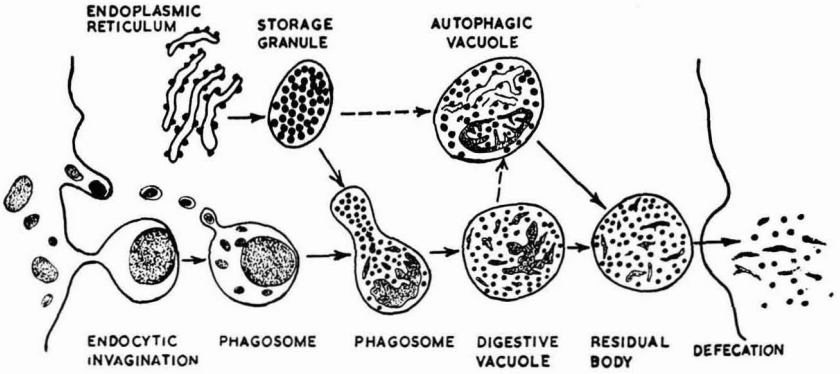

Fig. 2 — Types of lysosomes (as per de Duve[46] and Allison[23])

techniques[41]. Simultaneous biochemical and morphological studies of the lysosomes have been carried out on a few tissues like kidney[39], polymorphonuclear leucocytes and thymus[7,42]. These experiments confirm that every intracellular organelle, bounded by a single membrane and staining for acid phosphatase, could be considered as belonging to the lysosome group[28]. Additional support for this hypothesis has also come from the histochemical localization of β-glucuronidase[28], lysozyme[7] and nonspecific esterase[43] in these structures.

Functions

The possible functions of the lysosomes are circumscribed by the activities of their enzymes. These include soluble acid hydrolases capable of acting on the most important cell constituents. The working hypothesis will, therefore, be that lysosomes are involved in the process of acid hydrolysis. These may comprise digestion of foreign material engulfed by pinocytosis, athrocytosis or phagocytosis, physiological autolysis, which presumably occurs to some extent in all tissues, and particularly, as part of the more specialized processes of involution of mammary glands, metamorphosis, holocrine secretion, etc., pathological autolysis or necrosis and post-mortem biochemical reactions occurring in refrigerated, frozen and irradiated foods.

Intracellular Digestion and Engulfing Process

Physiological autolysis — Studies on the kidney lysosomes, also referred to as droplets[44], have revealed that substances like proteins are segregated inside the lysosomes by pinocytic activity. Brachet[45] has also shown that some of the dyes like neutral red and toluidine blue are localized in vacuoles resembling lysosomes. These findings strongly suggest an involvement of lysosomes in engulfing processes.

Autolysis occurs as a physiological process in the life history of some organisms, e.g. involution of thymus at puberty, of uterus after parturition, etc. It plays a major role in the metamorphosis of insects and some other zoological groups. During this process, the membrane of the primary lysosome simply dissolves, liberating enzymes to consume the cell constituents. This is believed to occur in the degeneration of corpus luteum of ovary[46] and regression of tadpole tail during metamorphosis[47,48]. Uretal ligation of the kidney[49] and perfusing liver with glycogen[50] have shown that lysosomes ingest some of the cellular organelles like ribosomes, mitochondria and Golgi vesicles to form a body known as autophagic vacuole. The contents of the autophagic vacuole thereupon are digested by the hydrolytic enzymes. This mechanism enables the cells to combat unfavourable conditions, wherein part of the cellular constituents can be broken down and its constituents utilized to provide energy or material needed to maintain the life of the cell. *In vitro* digestion of mitochondria, microsome and whole tissue, as shown by Sawant *et al.*[51] and Desai and Tappel[52], supports this belief.

Pathological Autolysis

Whatever may be the true physiological functions of lysosomes, it is a clear inference from the concept we have of these particles, that an excessive release of their enzymes within the cell may be associated with pathological and necrotic phenomena. These include attack on extraneous bacteria, tissue injury and inflammation, lytic and necrotic processes, immunity mechanisms, particle storage and carcinogenesis.

The experiments of Hirsch and coworkers[7,53] on polymorphonuclear leucocytes have indicated the involvement of lysosomes in combating bacteria by the mechanism of endocytosis. The digestion of ingested bacteria by leucocytes is an important form of defence against disease. But sometimes this mechanism fails to occur, since the bacteria have developed adaptations that enable them to survive lysosomal attack. Several bacteria are capable of killing leucocytes themselves due to their toxins, and others, including those causing tuberculosis, have thick waxy coats that resist the attack of lysosomal enzymes.

Uriuhara and Movat[54] have shown lysosomal involvement in causing tissue injury and inflammation. Freedman *et al.*[55] have confirmed this by suggesting the possibility of lysosomal mediation in this phenomenon. They attributed the cause to the release of lysosomal enzymes from degenerating leucocytes in the experimental rabbits. However, it is interesting to note the decreased lysosome fragility during wound healing. This fact has been demonstrated in the skin and oral mucosa of the mouse[56].

Brandes *et al.*[57-59] have studied the role of lysosomes in cellular lytic processes in detail. This has paved the way for successful curing of some tumours by chemotherapeutic agents. During the period of regression from treatment with the chemotherapeutic agent cytoxan, increased lysosomal activity with tumour cells was observed. The continued use of a lysosomal labilizer and the chemotherapeutic agent enhanced the antitumour effect. Hence, it is believed that lysosomes achieve this effect either by degrading the tumour cells or by enzymatic hydrolysis of cytoxan to an active form.

Many physical and chemical treatments are known to labilize the lysosomal membrane. Sudden deprival of oxygen[21], exposure to cyto-toxins of some kinds[60-62] and lipid solvents[63,64] are some of the conditions wherein the lipoprotein membrane gets ruptured completely, thus exposing the cellular constituents for breakdown. This results in the auto-digestion and necrosis of the cell. The released enzymes may also diffuse into the surrounding medium, damaging the extracellular structure. This explains the spontaneous fractures and other lesions caused by vitamin A intoxication[65].

It is recognized that lysosomes show a preference for the substances over which they act, depending on the cell in which they are situated. This property has led to the speculation that lysosomes play a role in eliminating antigens by the pinocytosis mechanism[66,67].

Increased availability of lysosomal enzymes has been shown to cause inflammations by the release of factors that increase the permeability of blood vessels, like histamine, serotonin and bradykinin[23,55,68]. In the case of gout, it was observed that the urate crystals are phagocytosed and the joints affected by gout produce pain, swelling and other symptoms[69]. There are many more inherited diseases in which the lysosomal system is ineffective either by lacking a key enzyme or by being incapable of performing complete digestion. In many of the 'storage diseases', e.g. the glycogen storage disease of children[70,71], even though phagocytosis takes place, complete digestion may not be possible and the metabolic products that should have broken down accumulate in pathological amounts.

Lysosomes can be involved in cell pathology in still other ways. Cells that are forced to engulf large amounts of foreign substances for the digestion of which they are not equipped will tend to accumulate such materials in lysosomes, possibly to the detriment of their general health. Plasma substitutes, such as dextran or polyvinyl pyrrolidone have been known to cause this condition[46]. It could also be involved in silicosis and asbestosis[23], diseases that result from the inhalation of silica and asbestos dusts respectively and their subsequent deposition in the lysosomes of the lungs.

Since lysosomes contain acid nucleases, their ability to breakdown DNA, the genetic material, has been studied widely[23] with respect to their possible role in malignancy formation. It has been known for many years that the chromosomal constitution of malignant cell is often abnormal. Allison[23] has presented a unifying hypothesis, implicating lysosomes in carcinogenesis. He suggests that radiation, oncogenic viruses and carcinogenic chemicals have a common action in causing damage to the lysosomal membrane, releasing the lysosomal enzymes which in turn attack the genetic material of cells. If the DNase enzyme can operate without impairing the capacity of the cells to divide, they could produce genetic changes resulting in somatic mutations, which lead to cancerous growth.

In addition to this, lysosomes have been shown to be involved in the storage of many carcinogens like benzopyrene and methyl cholanthene[23]. Recent reports indicate a key role of lysosomes in cancer formation in different tissues.

In recent years, evidence for the participation of lysosomes in the process of ageing is being slowly compiled. The lipofuscin age pigments develop from the ageing processes and knowledge about their composition reveals that they are of lysosomal origin[72]. This fact has been established since the peroxidized phospholipids, and membranes of mitochondria and endoplasmic reticulum have been shown to accumulate in lysosomes[73].

Properties of Lysosomal Membrane

From a review of lysosomal studies, it can be concluded that various factors could bring about intracellular alterations, causing damage to the lysosomal membranes. Duncan[74] has studied extensively the lysosomal membrane and has suggested some similarities between lysosomal membrane and membranes of cell, mitochondria, erythrocytes and plasma and also of nerves. Thines-Sempoux[75] has supported this belief and it is now suggested that the integrity of the lysosomal membrane is governed and maintained by an ATPase mechano-enzyme complex[74].

Studies of Weissmann and Thomas[76], Sawant *et al.*[77] and Weissmann[78] have shown that various factors are capable of altering the structure of the lysosomal membrane and releasing the hydrolases. Weissmann[78] has reviewed the role of various agents in labilizing and stabilizing lysosomes. The methods and agents that could alter the lysosomal membrane are listed in Table 2.

Various studies[76,78,79] have shown the possible control of physiopathological phenomena occurring in the cells by effective alteration of the membrane structure. Even though many investigations have been carried out to determine the status of lysosomes during a variety of stress conditions, the role of nutritional stress factors has not been fully understood. Conditions like starvation, administration of corticosteroids, exposure to X-irradiation, ingestion of protein-depleted or calorie deficient diets, are all known to impose active catabolism combined with acute negative nitrogen balance in animals. Even though lysosomes were examined during starvation[25], on exposure to X-irradiation[80], or after administering cortisone[62,81], their status and role under various nutritional stress conditions are not yet fully understood.

Table 2 — Methods and Agents Causing Labilization and Stabilizalion of Lysosomes*

Labilization	
In vitro:	Hypotonic conditions; freezing and thawing; low *p*H; cations; nonionic detergents; digitonin; blendorization; ultraviolet irradiation; X-irradiation; phospholipase; proteases; staphylococcal hemolysin; streptolysins O & S; progesteron and testosterone; diethyl stilbesterol; ediocholanolone and 5 β-H steroids; 5-β-H-bile acids; icterogenin, vitamin A; canthardine; cycteins; lysolecithin
In living cells:	Vitamin A; endotoxin; streptolysins O & S; ultraviolet irradiation; X-irradiation; 2,4-dinitropherol; antigen-antibody reactions; high oxygen excess; icterogenin; ischemia; anoxia; shock; prosphase of mitosis; endocytosis; metamorphosis and tissue resorption; virus infection; starvation; thyrotropin in thyroid
Stabilization	
In vitro:	Cortisol; cortisone; cholesterol; chloroquine; antihistamines; serum factors in autoimmunity; β-methasone; prednisone
In living cells:	Cortisone and analogues; chloroquine; serum factors in autoimmunity; 'tolerance' to endotoxin

*Based on the reports of Weissmann[78,104].

Effect of Experimental Stress Conditions on Lysosomes

Beaufay *et al.*[82] examined nutritional necrosis and de Duve and Beaufay[83] have studied ischaemic livers with respect to lysosomal enzymes. Desai *et al.*[84] have found raised activities of lysosomal

hydrolases in the breast muscle of chicks with nutritional muscular dystrophy. Tappel *et al.*[24] described similar trends in the acid hydrolases of the brain tissues of chicks with encephalomalacia. Roels *et al.* have shown that biological membranes become increasingly permeable in vitamin A deficiency[85]. Dingle *et al.*[86] and Weissmann *et al.*[87] have studied the effect of hypervitaminosis A with respect to chicken cartilage and guinea-pig liver lysosomes respectively. However, these studies only revealed the excessive release of the lysosomal enzymes and no attempt has been made to understand the exact mechanism governing the enzymes with respect to their binding. Bunyan *et al.*[88] have recently reported several experiments based on vitamin E deficiency. They examined the release of lysosomal enzymes during muscular dystrophy, encephalomalacia and exudative diathesis in chicks, gestation-resorption, liver necrosis and testicular degeneration in rats. The alterations in the release of enzymes were attributed to the generalized vitamin E deficiency. Dingle and coworkers[89] have studied the effect of vitamin A deficiency on the proteolytic activity of rat liver and kidney lysosomes. In another study[90], they examined rat kidney lysosomes under vitamin E deficiency. Umana[91] has reported alterations in liver nitrogen and proteolytic enzymes during protein deficiency. Deposition of glycogen is shown to occur in lysosomes during protein depletion in rats[92]. The effect of protein malnutrition has been studied extensively[93] in animals, in order to understand the correct picture imposed by protein depletion in man. These studies indicated that protein deficiency produces conditions known as 'protein-calorie malnutrition' in human beings. The enzyme levels of jejunal mucosa of rats were examined by Solimano *et al.*[94] during protein-calorie malnutrition. Stewart and Platt[95] have recently reported the influence of protein-calorie deficiency on the central nervous system.

In our laboratory, we have made an attempt to understand the status of lysosomes from the liver of adult protein-starved rats. The experiments were designed in such a way that calorie restriction was minimal. Since force-feeding and *ad libitum* feeding techniques are known to impose symptoms similar to kwashiorkor and merasmus respectively, spaced feeding or the single daily feeding method[96,97] was adopted during the course of these studies. It was shown that feeding of protein-free diet changed the characteristics of liver lysosomes. This has been indicated by the alterations in sedimenting properties, swelling of the membrane and structural freedom for lysosomal enzymes in liver homogenates as well as in isolated particles[98]. The observations of Adhikari *et al.*[99] on the elevation of vitamin A alcohol levels and damage to lysosomal membrane during protein deficiency confirm these findings.

Food Preservation and Lysosomes

Many investigations have been undertaken to effectively preserve perishable flesh foods, with minimum possible alterations in composition and acceptability of such stored foods. Several physical and chemical methods like storage at refrigeration temperature and freezer storage, coupling dehydration with cold storage and chemical methods like treating foods with a variety of chemical agents prior to storage have been used extensively in order to extend the storage life of flesh foods. In addition to these methods, radiation preservation of foods also has been studied by exposing the meats to ionizing radiations. The problems that could arise out of stored flesh foods are the tenderization, change in colour and texture, production of undesirable flavours and spoilage by microorganisms[100].

The spoilage of flesh foods stored at subroom temperatures and at freezing temperatures has been attributed to intracellular autolysis[101]. The autolytic enzymes comprise proteases, including lysosomal hydrolases[28]. These enzymes are known to tenderize the meats[101] and the hydrolytic products released may also influence the acceptability of the stored flesh foods. Since lysosomes are known to exist in all animal cells and because of the presence in them of hydrolytic enzymes, they are capable of digesting intracellular as well as extracellular materials[28]. The release of these enzymes occurs at a faster rate when the samples are stored at subroom temperatures[21]. Exposure to ionizing radiation has been shown to alter the membranous structure of the lysosomes, thus enhancing faster release of the enzymes[102,103]. Storage in freezer and subsequent thawing facilitates complete release of lysosomal hydrolases[21]. Hence, it is very important to consider the role of lysosomes in the preservation of flesh foods that are stored either in subroom temperature or in freezer.

In our laboratory, studies are in progress relating to the alterations in the lysosomal enzymes after subjecting chicken liver and muscles of fish to pasteurizing doses of gamma radiation. We have earlier identified the existence of lysosomal enzymes in both free and bound forms in muscles of *Tila-pia mosambica* (fresh water fish) and Bombay duck (sea water fish) fishes. Irradiation of fish muscle and chicken muscle facilitated quicker release of lysosomal hydrolases. However, it was established, at least in the case of chicken liver, that there existed a difference in the pattern of binding of these enzymes with the particulates, as evidenced by their differential release, which depended largely on the surrounding osmolarity. In the case of the muscle of Bombay duck fish, it was observed that the lysosomal enzymes were concentrated in the drip, during the course of storage.

Irradiation or freezing could cause release of lysosomal enzymes of fish muscle in the soluble phase and may then accelerate the degradation of macromolecules. This, in turn, could lower the water holding capacity of the tissue, thus explaining exudation of more drip after irradiation or freezing. It is known that treating fish muscle with polyphosphate solutions minimizes drip loss. The water holding capacity of Bombay duck fish muscle is enhanced by giving a single dip in solutions of sodium chloride or sodium polyphosphate. It is interesting to speculate that these pretreatments could promote lysosomal stability. Further work is needed to elucidate these effects and to

characterize the drip constituents in terms of degraded macromolecules like proteins and nucleotides in the muscle tissues.

Summary

The occurrence, distribution and properties of lysosomes as well as the recognized types of this subcellular organelle are reviewed. The general functions of lysosomes and their role in cellular autophagy and in combating or enhancing certain pathological processes, including carcinogenesis are summarized briefly. The response of lysosomes to a variety of physiological stress states is discussed. Their possible significance in preservation of perishable flesh foods by irradiation has been indicated.

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Effect of Ultraviolet Light on Nucleic Acids

B. B. BISWAS
Bose Institute, Calcutta 9

ULTRAVIOLET light has long been employed as a mutagenic agent in biological systems following the observation that the action spectrum of its effects coincided with the absorbance spectrum of nucleic acids[1]. The work which has perhaps created greatest stimulus was that of Beukers and Behrends[2] relating to the conversion of thymine to a dimeric product either in frozen solution of thymine or in aqueous solution of DNA. There is increasing evidence that the photoproducts of thymine other than the dimer, i.e. hydrated product, etc., are also produced both *in vivo* and *in vitro*. The lowering of the melting temperature change in helix coil transition, uptake of formaldehyde by DNA and density increase in cesium chloride after UV irradiation have been well demonstrated. The dose of UV radiations required to reduce the molecular weight by 50% was about 2×10^5 ergs/mm^2, while that to reduce the transforming activity of the streptomycin marker in this DNA to the same extent was only about 3×10^3 ergs/mm^2. From the consideration of the structure of DNA proposed by Watson and Crick it is obvious that adjacent thymines in a DNA strand are not optimally arranged to permit thymine dimerization. One or both of the thymines must rotate somewhat so that their rings can superimpose. For this, streching or disorganization of the hydrogen bonded backbone of DNA should occur which might be due to hydration of adjacent cytosine residues. The following types of interactions under the influence of UV light have also been reported. Recent findings on the photochemistry of nucleic acids have been reviewed by Shugar[3], Wacker[4] and Smith[5].

Intermolecular Crosslinking of DNA after UV Irradiation

After UV irradiation long fibres of DNA were formed on subsequent contact with water or salt solution. These fibres were completely insoluble even at elevated temperature and were also resistant to the action of DNase[3]. A dimerization mechanism similar to that of thymine dimer has been suggested[5]. The mechanism is probably due to the chemical interaction of pyrimidine groups on different molecules brought into juxtaposition by removing the water lattice that normally holds them apart. It is questionable how much of a role this phenomenon would play in a normal cell, but the state of hydration does appear to be of importance in the irradiation of bacteria and viruses.

Intramolecular Crosslinking of DNA

After irradiation of DNA with a dose of 2×10^6 ergs/mm^2 a considerable portion of it was altered in such a way as to prevent the subsequent strand separation of DNA by heating or treating with formaldehyde which otherwise was possible. The strands were apparently crosslinked by the action of UV light. For a given dose of UV the extent of crosslinking increased for different samples of DNA proportional to the adenine-thymine (AT) content of the DNAs[6]. The DNA in which almost all the thymine was replaced by bromouracil was about five times as sensitive to interstrand crosslinking by UV as was normal DNA. This seems to exclude the normal thymine dimer as being involved but to exclude the involvement of

thymine by some other mechanism[7]. It has also been argued that the formation of interchain dimers may require local opening up of the helix structure to allow the bases to assume proper orientation. This crosslinking has been found to be favoured as the temperature is raised. Maximum crosslinking has been obtained at a temperature where denaturation is only 20%.

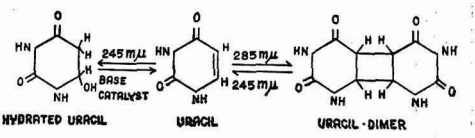
Crosslinking of DNA to Protein

It has also been reported that there is a progressive decrease in the amount of DNA that can be extracted with detergent from bacteria and other cells following increasing doses of UV, indicating that DNA is crosslinked to protein. Further proof came from experiments showing that DNA and protein could be crosslinked *in vitro*[5]. If DNA was irradiated in the presence of serum albumin and then submitted to the DNA isolation procedure there was a progressive loss of DNA with increasing dose of UV. Furthermore, this crosslinking phenomenon can be abolished by the treatment of the cells with trypsin. The importance of this mechanism has not yet been known but this crosslinking generally occurs at a sublethal dose of UV light.

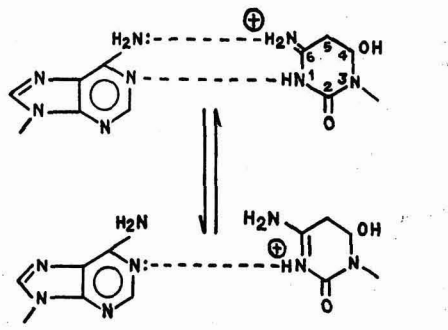
Ribonucleic Acid and UV Light

Not only is DNA the target material but RNA has also been affected. Irradiation of RNA from TMV with fairly high doses results in complete destruction of viscosity as well as a loss in the ability to stain metachromatically, indicating perhaps a molecular degradation[8]. The inactivation of infectious RNA from tobacco mosaic virus (TMV) is highly resistant to further irradiation[9]. Studies have also been extended to different types of RNAs and also polyribonucleotides including oligonucleotides. Dimer and hydrated products of uracil have also been isolated[10]. Grossman[11] demonstrated that hydration appears to predominate in poly U at 245 mμ, while dimer formation predominates at 285 mμ and has shown that dimers in poly U can be reversed by reirradiation at 245 mμ as is the case with thymine dimers (Scheme 1). Poly A and poly G are more resistant to UV irradiation.

Different amino acid acceptor RNAs have been found to be differentially sensitive to UV doses. This differential sensitivity may be dependent on the 5-ribosyl uracil content. It has been proved that triple UUU codes for phenylalanine and UUC for serine but after UV treatment of poly U, incorporation of serine in a protein synthesizing system is increased, indicating that UV irradiation has somehow changed UUU to some configuration that resembles UUC. The chemical alteration responsible for this phenomenon appears to be hydration rather than dimer formation. Poly C similarly irradiated appears to lose proline (CCC) incorporation, whereas stimulation of serine (UUC) and leucine (UUC or UCC) occurs[12]. Furthermore, poly C directed GTP incorporation by RNA-polymerase is influenced by UV light allowing also ATP incorporation and the transition occurring in these cases is from C to U (ref. 13). The three photoproducts of cytosine, viz. (i) deaminated cytosine (uracil), (ii) dimer, and (iii) hydrated product, have been studied. The



Scheme 1 — Photoproducts of uracil



Scheme 2 — Hydrogen bonding properties of protonated cytosine hydrate

hydrogen bonding properties of protonated cytosine hydrate, as indicated in Scheme 2, may be responsible partially for the transition in the transcription and translation process. It has also been shown that irradiation energy of the order of $3{\cdot}5 \times 10^4$ ergs/mm^2 drastically reduces the capacity of ribosomes for the incorporation of amino acids into protein[14]. The question may be to correlate the inactivation of nucleic acids with the energy of UV light.

Repair of DNA

The recovery process associated with UV irradiation of DNA is supposed to involve the partial degradation of the regions containing photoproducts, such as thymine dimers and their subsequent repair replications[15]. Repair of UV damaged bacterial DNA has been shown to take place by two different mechanisms: (i) monomerization of pyrimidine dimers by the action of an enzyme and light (photoreactivation) and (ii) enzymatic excision of pyrimidine dimers from the bacterial DNA in the absence of light, presumably followed by repairs of the holes produced by the excision (dark repair). Photoreactivation involved the action of an enzyme that is selectively bound to DNA that has been irradiated with UV light; when this enzyme is activated by visible light it cleaves the pyrimidine dimers, thereby restoring the two bases to their original form. Photoreactivation is thus a repair process that can be turned on or off merely by flicking a light switch. The dark reactivation can be turned off genetically, by finding mutant strains of bacteria that lack the repair capabilities of the original resistant strain. The same recovery process is assumed to operate in the repair of UV induced lesions in phage DNA through the action of bacterial enzymes, i.e. host cell reactivation (HCR). It has been demonstrated that HCR can selectively be inhibited by caffeine. The action of caffeine seems to depress the excision of pyrimidine dimers from UV irrodiated DNA,

i.e. caffeine inhibits the degradation of UV irradiated bacterial DNA and of UV irradiated λ phage DNA upon entering the host bacteria[16,17]. There is at present no proof that any other UV induced change in DNA can cause lethal effects nor can one exclude the possibility that all lethal effects in bacteria of normal UV sensitivity are the result of pyrimidine dimers. There is, however, evidence that protein damage may be important in the extremely resistant *Micrococcus radiodurans*[18]. In the spores of *Bacillus megaterium*, UV lesions involving different photoproducts are produced in DNA in comparison to those in vegetative cells. The spore photoproducts disappear from the DNA and do not appear in the medium, suggesting that DNA in spores is in a form different from that found in vegetative cells[19].

UV induced pyrimidine dimers have been found to be lost from DNA in the case of HeLa cells. There are some similarities between the reaction of human cells to UV irradiation and UV repair mechanism in bacteria. But other mammalian cells examined have failed to show any indication of such a phenomenon and human cells seem to be exceptional in this respect[20].

Quantum Yields for Inactivation of Nucleic Acids*

Since 99% killing dose of *Esch. coli* dimerizes only 0·1% of the total thymine (only 25% thymine in this DNA) and since at least 50% of the action of UV on transforming DNA can be accounted for by thymine dimerization, only about 0·025% of the molecule of DNA has been photochemically altered by a UV dose that kills 99% of the bacterial population. The chemical data available on the UV inactivation of DNA and also RNA suggest that the irradiation damage is highly localized. The low quantum yields for the inactivation of the nucleic acids (10^{-3}-10^{-4}) also support this idea[3,5]. The quantum yield for a particular nucleotide is very sensitive to the base sequence in a polynucleotide chain. That for poly T varies markedly during the course of photolysis. The initial rate of photolysis proceeds with a quantum yield (12×10^{-3}) comparable in magnitude to that for poly U or poly C. The purine nucleotide residues in both poly A and poly G are more radiation resistant than the free nucleotides; the quantum yield is about $0{\cdot}5\times10^{-4}$. The photochemistry of the twin stranded complex of poly A and poly U differs significantly from that of poly U alone; the quantum yield of uridylic acid in the complex is about 25-fold less than in poly U. Increasing efforts are now being directed in isolating the different photoproducts of different bases and polynucleotides in order to put forward some explanations for the changes UV or visible light can induce. Though light is essential for sustaining life on this earth yet it constitutes a threat to the cellular organization through the unwanted photochemical reactions discussed above. So, the effects of these photoproducts of nucleic acids on the biological activity are just beginning to be understood and most probably in future more exciting informations will be unravelled.

*1 quantum = $7{\cdot}8\times10^{-12}$ ergs at 253·7 mμ. A quantum is a unit of light energy; the energy E in quantum is given by the expression hc/λ, where h is Planck's constant; c. the velocity of light; and λ, the wavelength.

Summary

Ultraviolet light has several effects on nucleic acids. Among them the most common is the dimerization of thymine or uracil. The hydrated products of thymine, cytosine and uracil are also detected. Crosslinking of DNA with protein has been reported. There may be other defects as well produced after UV irradiation but nothing is known with certainty how far these play a role in the inactivation of nucleic acids. The hydrogen bonding properties of protonated cytosine hydrate are responsible partially for the transition in transcription and translation process. The repair of UV damaged bacterial DNA has been shown to take place by two different mechanisms: (i) monomerization of pyrimidine dimers by the action of enzyme and light (photoreactivation), and (ii) enzymic excision of pyrimidine dimers in the absence of light, presumably followed by repairs of the holes produced by excision (dark repair). These aspects have been discussed in the light of recent findings.

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REVIEWS

FORECAST 1968-2000 OF COMPUTER DEVELOPMENTS AND APPLICATIONS, coordinated by Chresten A. Bjerrum (Parsons & Williams, Copenhagen), 1969. Pp. 64. Price $ 12.50

The publication under review analyses and evaluates the social and technical implications of computer development in the next 32 years. The method used is the so-called Delphi technique based on intuitive judgements as a result of two questionnaires circulated to the participants of FILE 68, an international seminar on FILE organization held in Denmark in November 1968. Thus, the forecast is in a way the distillation of the opinions of 250 delegates from 11 countries who participated in FILE 68. Twenty-four questions regarding the effect of computer development in the fields of sociology, labour, politics, commerce, education, technology and industry are documented and evaluated.

Some of the major findings of the forecast are: (1) A 50% reduction of the labour force in present industry is expected by the late 1980's. The reduction will be partially compensated by shorter working hours and by absorption of workers by new industries; but the problem of unemployment is expected to be much more serious in the future than it is today. (2) In the year 2000, all major industries will be controlled by computers. Small industries will not be automated to the same extent, nor is it expected that many will exist by then. (3) The influence on the medical profession by EDP is expected to be extensive. By 1975, treatment of patients in major hospitals will be controlled by computers and by 1980's a majority of doctors will have EDP terminals for consultation and will be able to give reliable diagnosis by computer. (4) The future software will, to a large extent, be built into the hardware by late 1990's and computers which learn from their own experience will exist before 1989. (5) In spite of advanced technology, computer prices are expected to decrease by a factor of 100 by the end of 1980's.

RESEARCH IN PROGRESS: Vol. 1 (Inter-University Board of India and Ceylon, New Delhi), 1968. Pp. xvi+429. Price Rs 40.00

In August 1965, the Inter-University Board of India and Ceylon decided to resume publication of its two projects ' Bibliography of theses accepted ' and ' Research in progress '. The volume under review concerns the second project related to the collection of information about research in progress. The period from 1958 to 1966 has been taken as the base period. It is visualized to be an annual feature. The present volume deals with only physical sciences and covers 1947 entries. These have been classified by the Dewey decimal classification and govern the general arrangement. Each entry includes detailed particulars about the scholars in the following order: serial number, name of the scholar, title of thesis as registered by the university, name of the university, department or institute where research work is conducted, the period of research programme, name and designation of the guide, a brief résumé of research topic and the reference note. The serial number consists of two parts. The first is the serial number that runs through the length of the publication and is indicative of the total number of entries listed, while the second indicates the serial number of the entries within a particular subject. This will enable one to assess the quantum of activity in a particular area. Universal decimal classification has been used for the identification of these topics. The classification number has been given at the bottom of each entry on the extreme right-hand side. While alphabetic subject is given in the beginning, the volume ends up with the scholar index.

The Secretary of Inter-University Board of India and Ceylon writes in the preface that " The information provided in this and subsequent volumes is complete only to the extent that the universities could be persuaded to make it available ". It is needless to emphasize that the cheerful cooperation of the universities and institutions of higher learning on the one hand and the publishers (Inter-University Board of India and Ceylon) is indispensable to make this laudable effort successful. In spite of this, there could be considerable amount of omission in such a compilation. It has been very much surprising for the reviewer to find that out of about 250 Ph.D. theses put forth during this period (1958-66) from his own institution, only a few (3 or 4) get mentioned in this present volume. It is also rather strange that a subject like biochemistry does not find a place even in the alphabetic subject index. We hope that all these shortcomings will be overcome in the coming days and we look forward for subsequent publications to get the collected information about the progress of research in India.

A.R.V.

ORGANIC FUNCTIONAL GROUP ANALYSIS by George H. Schenk (Pergamon Press, Oxford), 1968. Pp. vii+297. Price 30s.

The book under review consists of two parts. Part I deals with the determination of functional groups, namely carbonyl, hydroxyl, amino, alkoxy silanes, epoxides, etc. The novelty of this book is that the author has not only discussed the recent developments of analytical methods for organic functional groups, but has given a survey of the earlier methods of the determination of the above functional groups with appropriate comments. The rates of reactions have been discussed as well. The optimum conditions have not been merely mentioned. The author has taken great pains to go deeply into the principles behind the maintenance of the optimum conditions for every single reaction he has described. Mechanic interpretations have been given wherever possible and ample reading references have been provided.

Part II deals more with quantitative estimation and spectral analysis of various functionalities and has been dealt with as efficiently as Part I.

Lastly, each chapter ends with the instrumental method of analysis.

The book has a good format and the presentation is quite lucid. The approach in presenting the materials is somewhat novel and the latest developments in the field along with the references have been included.

This book is ideal as a reference guide for undergraduate and postgraduate students.

A.C.

HALIDES OF THE LANTHANIDES AND ACTINIDES by D. Brown (John Wiley & Sons Inc., New York), 1968. Pp. x+280. Price $ 11.00

This book is one of the volumes in a series entitled 'Halides of the transition elements'. The text is divided into five chapters and three appendices.

Chapter 1 gives a summary of the known halides and oxyhalides of the lanthanides and the actinides, together with those of lanthanum and actinium which are really the precursors of these two series respectively. The elements scandium and yttrium have very close chemical analogies to the lanthanides, and their halogen compounds are also discussed. The compounds (halides and oxyhalides, including the complex halides) corresponding to the different oxidation states of these elements, the relative stabilities of the various oxidation states and of the halides of each series have also been discussed rather briefly. As a logical sequence mention has been made of the lanthanide and actinide contractions, which have also been nicely represented diagrammatically (Fig. 1.1). Reference has also been made of the methods used to prepare and study the halides, etc., of these elements in sub-microgram quantities. Problems involved in the studies of the compounds of the strongly radioactive members of the actinide family have also been mentioned.

Methods of preparation and properties (both physical and chemical) of all the known halides, oxyhalides, and double halides and oxyhalides (i.e. complexes of these with the halides of other cations) corresponding to each of the halogens fluorine, chlorine, bromine and iodine have been discussed fairly elaborately in Chapters 2, 3, 4 and 5 respectively. Crystallographic and structural data have also been given wherever known. Original literature references have been quoted rather exhaustively, including some of the early 1968 publications. Thus, Chapter 2 (on the fluorides and oxyfluorides) covers 83 pages of actual discussion with 458 original references.

Informations available on the mixed halides (having more than one halogen) of uranium and protactinium (only one such compound of Pa is known so far) are compiled in Appendix C, which is preceded by Appendices A and B containing very useful data on the thermochemical properties of and metal-halogen and metal-oxygen vibration frequencies in the lanthanide and actinide halides.

The author has made a very commendable attempt to present the existing state of knowledge in the field in a handy volume, which will definitely be useful to all the advanced students and research workers interested in the subject.

Although materially not very important, it may be mentioned that in the text the author has preferred to refer to the oxidation state of the parent element in a compound by expressions like samarium (III), uranium (VI), neptunium (V), hexachloroplutonate (IV), etc. This is contrary to the usual convention in which these are written as samarium(III), uranium(VI), neptunium(V), hexachloroplutonate(IV), etc., where the oxidation state is indicated within parentheses in proximity with the name (or symbol) and is not written separately as has been done by the author. The omission of an author index is also regrettable.

D. BANERJEA

LABORATORY MANUAL OF PEDIATRIC MICROBIOCHEMICAL TECHNIQUES, Fourth Edition, edited by Donough O'Brien, Frank A. Ibbott & Denis O. Rodgerson (Harper & Row Publishers, New York), 1968. Pp. xiv+367. Price $ 11.90

The increasing demand by clinicians for simple and reliable laboratory investigations for diagnostic purposes has necessitated the introduction of new books on this subject and frequent editing of the older ones. This is particularly so in pediatric practice where rapid strides have been made in the understanding of the biochemical basis of congenital disorders and of other diseases of the newborn due to the availability of advanced biochemical techniques and instrumentation. The authors of the book under review deserve to be congratulated for bringing out this new edition which incorporates methods that are in such great demand in pediatric diagnostic procedures.

In the revised edition of the manual, the authors have introduced some of the latest microchemical methods, discussing the usefulness of each and comparison of merits wherever alternative methods are available. The methods are listed in an alphabetical order and each technique begins with a clinical and/or a technical commentary and ends up with a list of references to original research papers. Normal values have been included and, wherever possible or necessary, alterations of tables and figures have been effected. The authors have limited their scope of discussion to pediatrics and unnecessary details have been omitted. For example, although a detailed discussion of the methodology and of the biochemical basis of the investigation in question would be welcome, the purpose of the book would have been lost through its becoming too unwieldy. Cognizance is taken of the chemical background of the pediatrician and tables of standards like atomic weights, molecular weights and useful details of solvents and reagents in common use have been included.

The fourth edition, as the authors maintain in their preface, has retained the original simple format of the previous ones, while greatly expanding the clinical commentary and introducing special sections to appropriate screening and diagnostic tests for mental retardation, the red cell enzyme defects and the glycogen and lipid storage diseases. While

the inclusion of techniques for the estimation of various poisons likely to be met with in pediatric practice would definitely have been quite helpful, the authors have relegated this to bigger and conventional works of clinical chemistry. The same can be told of the omission of techniques for steroid estimation.

The real merits of this book are of course its simplicity and its speciality, and as such it can serve as a useful desk reference in any clinical biochemistry department attached to the pediatrics where it can serve as a useful guide to the technician, clinician, and the chemist.

T. N. SEKHARA VARMA

B-P-H (BOTANICO-PERIODICUM-HUNTIANUM) edited by G. H. M. Lawrence, A. F. Gunther Buchheim, G. S. Daniels & H. Dolezal [Hunt Botanical Library, Pittsburgh (Pa), USA; Distributors: S-H Service Agency Inc., New York], 1968. Pp. 1063. Price $ 30.00

This new publication is a compendium listing nearly 12,000 titles of world periodical literature on plant sciences, for purpose of reference by botanists and other scientists interested in plant sciences. It catalogues all periodicals that contain not only papers of purely botanical interest, but also those partly botanical in scope, viz. those dealing with agriculture, bacteriology, biology, forestry, genetics, geography, microbiology, microscopy, pharmacology, etc. It includes also a number of medical and other general science periodicals, particularly those issued in the last century and which contained many articles on botanical aspects. The list excludes, however, publications like proceedings of congresses, symposia, etc., though they often contain information of botanical importance. The book also excludes such popular periodicals as bulletins, circulars, etc., which do not include original material. For purposes of this bibliography, a periodical has been defined as a publication that is issued in successive numbers at regular or irregular intervals and is intended to continue indefinitely.

The main text of the volume provides the following information about each periodical: (a) an internationally acceptable unambiguous abbreviation of the title; (b) the full title as given on the title page of the first volume; (c) the place of publication of the first volume; (d) the volumation and pertinent publication dates; and lastly (e) index reference for the titles as given in *Union List of Serials*. Besides acceptable abbreviations for the periodicals, in many instances, abbreviations already used in botanical literature are given as synonyms, in order to guide research workers using some of the older and classical works when the modes of citations were not standardized.

The entire text has been produced by photo-offset lithography based on computer-processed print-out. Periodicals in more than 45 languages have been indexed, the accuracy and completeness of their titles being assured by a large body of botanists in various countries who have collaborated with the editors, particularly on works of oriental and eastern European origin. A special type font has been designed for this project, giving capital and lowercase letters, together with conventional accent marks required in some of the languages represented.

Besides the text, there are two appendices, one bringing together abbreviations of words used in abbreviating titles and the other, a list of language equivalents for geographic names often found on the title or imprint of periodicals. The entire work has been admirably executed by the members of the Hunt Botanical Library in collaboration with a large body of botanists, documentationists and linguists in various institutions, in USA and Europe.

The book is well printed and produced and is sure to be welcomed by all botanical institutions and botanists throughout the world, as a handy reference work, particularly to those who cannot afford the *World List of Scientific Periodicals*. The Hunt Botanical Library deserves the gratitude of all interested in plant science literature, for sponsoring this valuable compendium.

K. R. RAMANATHAN

PUBLICATIONS RECEIVED

BEHAVIOUR AND ULTIMATE STRENGTH OF REINFORCED CONCRETE IN SHEAR by V. Ramkrishnan (Postgraduate College of Technology, Coimbatore), 1969. Pp. vi+106+xxiv. Price Rs 25.00

ORGANIC COMPOUNDS OF LEAD by Hymin Shapiro & F. W. Frey (Interscience Publishers Inc., New York), 1969. Pp. xiii+486. Price $ 18.00

INVENTORS HANDBOOK by Terrence W. Fenner & James L. Everett (Chemical Publishing Co. Inc., New York), 1969. Pp. xi+309. Price $ 7.50

HEME AND CHLOROPHYLL — CHEMICAL, BIOCHEMICAL AND MEDICAL ASPECTS by Gerold S. Marks (D. Van Nostrand Co. Ltd, London), 1969. Pp. xiii+208. Price 75*s*.

NORMALE UND PATHOLOGISCHE PHYSIOLOGIE DER NIREN by P. Bálint (Veb Verlag Volk Und Glesundheet, Berlin), 1969. Pp. 354

PHYSICAL METALLURGY OF IRON AND STEEL by Rajendra Kumar (Asia Publishing House, Bombay), 1968. Pp. xi+456. Price Rs 35.00

LECTURES ON INTEGRAL EQUATIONS by Harold Widom (D. Van Nostrand Co. Inc., New York), 1969. Pp. x+113. Price $ 3.50

LECTURE SERIES IN DIFFERENTIAL EQUTAIONS: Vol. 1, edited by A. K. Aziz (D. Van Nostrand Co. Inc., New York), 1969. Pp. viii+199. Price $ 4.50

THE PHILOSOPHICAL IMPACT OF CONTEMPORARY PHYSICS by Milič Čapek (D. Van Nostrand Co. Inc., New York), 1961. Pp. xii+419. Price $ 8.00

INVARIANT MEANS ON TOPOLOGICAL GROUPS by Frederick P. Greenleaf (D. Van Nostrand Co. Inc., New York), 1969. Pp. x+113. Price $ 3.00

NOTES & NEWS

New Reststrahlen band behaviour in mixed crystals

A new type of mixed crystal behaviour in the case of infrared reflectivity spectra of $Ga_{1-x}In_xAs$ single crystals has been reported by M. H. Brodsky of the Night Vision Laboratory, Virginia, and G. Lucovsky of Case Western Reserve University, Ohio. The spectra in this case are characterized by the occurrence of two Reststrahlen (RN) bands, a strong band which is shifted down in frequency monotonically out of the GaAs RN region to the edge of the InAs RN region with increasing molar, fraction of InAs (i.e. increasing x) and a lower frequency weak band which occurs in the InAs RN region. Previous workers had distinguished two types of behaviour in similar mixed polar crystals. Alloy crystals such as $Na_{1-x}K_xCl$ and $Cd_{1-x}Zn_xS$ have been reported to exhibit a single RN band for all values of x- 'one-mode' systems. The frequencies characterizing this band are observed to be intermediate to those of the end members and shift monotonically with composition. In contrast to this, 'two-mode' behaviour, where two reflection bands are observed, occurs in crystals such as $GaAs_{1-x}P_x$ and $CdS_{1-x}Se_x$. For each band, the frequencies of the optic modes lie approximately within the RN region of the end member constituent compounds ($x = 0$ or 1); however, the strength of each band varies with the composition. The behaviour now reported represents a third and a new type of mixed crystal RN band response which is intermediate to that observed in the one- or two-mode systems. This new type of behaviour was observed in a series of studies on the room temperature reflection spectra of $Ga_{1-x}In_xAs$ taken in the form of epitaxis films of varying thicknesses.

It was observed that one set of frequencies [belonging to both transverse and longitudinal optic (TO_1 and LO_1)] shift smoothly with composition, decreasing respectively from the GaAs TO and LO frequencies and shifting out of the GaAs RN band towards the InAs LO frequency with increasing InAs content (increasing x). The second set of frequencies (TO_2 and LO_2) lies within the region of the InAs TO and LO for all compositions. This behaviour of the optical power modes of $Ga_{1-x}In_xAs$ is quite different from that observed in other known mixed crystals. Specifically, in two-mode systems, e.g. $CdS_{1-x}Se_x$ in each branch, the LO frequency increases as one moves away from the respective low concentration gap and localized modes. In contrast to this, in a typical one-mode system, both frequencies shift in the same sense as the composition range is traversed. In the new type of RN band response, the low frequency band behaviour (TO_2 and LO_2) is two-mode like, whereas the high frequency band behaviour (TO' and LO') is one-mode like.

The phenomenological criterion in a mixed crystal system represented by $A_{1-x}B_xC$, where the atomic mass of A is less than that of B) for a two-mode behaviour, was postulated as the LO and TO frequencies being degenerate, in the limit of small concentrations, at the local (above the optical branch of BC) and a gap-mode (between the acoustical and optical branches of AC) frequency. If this frequency is not distinct from the RN band of the host crystal, then the second mode does not form. The criterion for one-mode behaviour would be that neither a gap nor a localized mode exists in small concentrations. In the intermediate case, in crystals such as $Ga_{1-x}In_xAs$, the criteria are not satisfied for either behaviour and, therefore, a third type of behaviour is observed.

The conditions necessary for this type of intermediate or 'mixed-' mode behaviour would be (1) the absence of an energy gap in the phonon spectrum of the lighter compound and (2) the occurrence of nonoverlapping RN bands [*Phys. Rev. Lett.*, **21** (1968), 990].

New method of resolving NMR structures

A new method of resolving NMR structures in solids has been reported from the Department of Physics, Saint Louis University, Missouri.

In a diamagnetic solid consisting of concentrated nuclear spins and dilute paramagnetic electron spins where the two types of spins are loosely coupled through the electron-nuclear dipolar interaction, it is observed that the NMR spectrum, observed in the conventional thermal equilibrium NMR experiments, does not show any resolved quadrupole structures. This is due to the fact that the rigid-lattice dipolar linewidth of each absorption line is roughly the same as the separation between two satellite lines. Hence, the NMR spectrum appears as a single broadened absorption line due to the rigid-lattice line broadening effect. It has been reported recently by R. K. Sook Lee and coworkers [*Phys. Lett.*, **26A** (1968), 572; *Phys. Rev. Lett.*, **21** (1968), 515] that the saturation of the centre of inhomogeneously broadened ESR line would give rise to a nuclear polarization with certain special features. An analysis of the characteristics of these nuclear polarizations has shown that the NMR quadrupole and/or dipole structures which are completely unresolved in thermal-equilibrium NMR spectra get resolved under dynamic nuclear polarization produced by saturating the centre of an inhomogeneously broadened ESR line.

Investigations of NMR spectra under the indicated dynamic nuclear polarization experiment not only yield the sign of the quadrupole constant, but also provide, thus, a new method of resolving the unresolved NMR structures.

There are a number of cases in solids, where the NMR spectra, observed in the conventional thermal equilibrium NMR experiments, do not show any resolved structures due to the line broadening effects, even though the nuclear spin system undergoes a quadrupole and/or dipole interaction. The application of the dynamic polarization method may enable one to resolve these structures,

thereby carrying out more effective and detailed NMR investigations in various types of solids.

One important aspect to be considered in the application of this method is the cross-relaxation among various NMR component lines, since they substantially overlap each other. If the cross-relaxation is strong the resultant thermal contact among various NMR component lines tends to equalize their nuclear polarizations; this results in a considerable reduction in NMR intensity of those component lines which are expected to be observed under the dynamic nuclear polarization experiments. This difficulty, however, may be overcome by making the dynamic nuclear polarization rate much faster than the cross-realization rate, by employing a high microwave pumping power [*Phys. Rev. Lett.*, **21** (1968), 1627].

Time-resolved spectroscopy

A new equipment and two techniques developed at the Hirst Research Centre of the General Electric Co. Ltd, UK, make it possible to observe transient changes in the quantity and quality of the light emitted or absorbed by a material or device. With the use of these techniques which enable the measurement of transient changes on a microsecond time scale and with a spectral bandwidth 1 Å, it would be possible to study those characteristics of a system under investigation, which normally could not be observed in ordinary spectroscopic studies.

The equipment consists of a high resolving power prism monochromator and a wide spectrum range photomultiplier calibrated with standards of spectral intensity in the range 2000-9000 Å. With the aid of a high speed oscilloscope, measurements of the variation of intensity with time and wavelength can be made on repetitive transient phenomena.

There are two possible ways of operating the system. In one, the monochromator is set to successive wavelengths and the variation of intensity with time at each wavelength is displayed on the oscilloscope. This technique has been applied to the evaluation of the fluorescence spectrum excited in ruby rods, determination of the concentration of mercury atoms in a high power mercury-arc converter valve, and similar problems. In the second method, the oscilloscope is used to select successive time intervals and the monochromator is driven continuously to scan the spectrum. In this case, the variation of intensity with wavelength at a particular time is displayed on a potentiometric recorder. The time selection is made by coupling a signal from the oscilloscope to an electronic gate incorporated in the circuit to the recorder. Measurement of the electroluminescence spectrum emitted by silicon carbide lamps is an example of the problems which could be tackled by this method. A control circuit has also been constructed to drive the monochromator scanning mechanism in discrete steps to allow time for counting a statistically significant number of photoelectrons at each wavelength in the spectrum under investigation [*GEC-AEI J. Sci. Tech.*, **35** (1968), 124].

A new synthesis of 19-nor-steroids

A convenient synthesis of 19-nor-steroids involves the Birch reduction of steroids containing phenolic ring A, the latter class of compounds being obtainable by dienone-phenol rearrangement. In the case of aromatization of cross-conjugated di- or trienone, the 19-methyl group remains intact as substituent in ring A and subsequent reduction affords a mixture of products containing α- or β-methyl substituent. The removal of aromatic 19-methyl group has now been achieved in two steps.

The method involves the conversion of the aromatic methyl group into an aldehyde using ceric ammonium nitrate in aqueous acetic acid. With this reagent, aliphatic methyl groups, activated methylene groups and methoxy and acetate groups remain unoxidized. It is essential to adjust the reaction time for oxidation so that no over-oxidation occurs. The aldehyde obtained is directly for the decarboxylation reaction. This route to 19-nor-steroids has been demonstrated on three compounds, namely androst-1,4,6-trien-3,17-dione, 17β-acetoxyandrost-1,4,6-trien-3,17-dione, 17β-acetoxyandrost-1,4,6-trien-3-one and cholesta-1,4,6-trien-3-one [*J. chem. Soc.*, (1968), 2915].

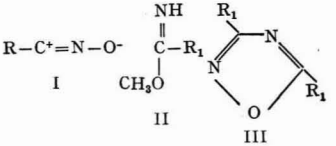
A new route to cyclobutenes

A new and facile synthesis of cyclobutenyl hydrocarbons from 1,2-divinylcyclobutane, which may be prepared by photolytic or thermal dimerization of butadiene, has been reported. 1,2-Divinylcyclobutane was heated to 80°C at a pressure of 620 lb/(sq in.) with ammonia and sodium amide, and the products were isolated by vacuum distillation after 30 min. 1,2-Diethylidenecyclobutane (λ_{max} 251 mμ; log $\epsilon = 4{\cdot}176$) and 1-ethyl-2-vinylcyclobutene (λ_{max} 243 mμ; log $\epsilon = 4{\cdot}278$) were obtained in 72 and 18% yield respectively.

For getting 1,2-diethylcyclobutene, 1,2-diethylidenecyclobutene was introduced dropwise in ammonia containing dissolved sodium at −33°C. After 60 min the mixture was quenched and on vacuum distillation afforded 1,2-diethylcyclobutene in 44% yield. The NMR spectrum of 1,2-diethylcyclobutene shows a sharp singlet superimposed on a quartet between 7·72 and 8·30 (8H) and a triplet centred at 9·03 (6H) [*Chemy Ind.*, (1969), 269].

A general method for the preparation of 3,5-disubstituted 1,2,4-oxadiazoles

A simple method for the construction of 1,2,4-oxadiazole ring system (III) has been developed, involving the reaction between aliphatic and aromatic nitrile oxides (I) like pivalonitrile and 4-chlorobenzonitrile oxide, and methyl imidates (II).

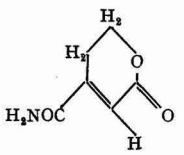


For the formation of oxadiazole ring system, it is possible that the nitrile oxide (I) attacks the imidic

esters to form the oxadiazoline intermediate which then loses elements of alcohol to furnish the oxadiazole. The reaction is facile with unreactive nitriles also, provided they are first converted into the corresponding imidic esters. This observation precludes the dissociation of imidic ester to nitrile and methanol followed by the addition of nitrile oxide to the nitrile thus generated, as one of possible routes for the oxadiazole ring formation [*Tetrahedron Lett.*, (1969), 311].

Gentiocrucine — A new nitrogenous substance related to mevalonic lactone

A new nitrogenous compound, gentiocrucine ($C_6H_7No_3$), related to mevalonic lactone has been isolated from *G. cruciata*. Structure (I) assigned to gentiocrucine has been arrived at on the basis of IR, mass and NMR, and chemical evidence.



I

It has a conjugated lactonic carbonyl group (1705 cm^{-1}), an NH_2 group (3480 cm^{-1}), a conjugated carbonyl (1642 cm^{-1}), a conjugated double bond (1622 cm^{-1}), and an ether linkage (1110 cm^{-1}). It exhibits a pair of triplets at 2·58 and 4·40 ppm for a $-CH_2-CH_2-$ group adjacent to a quaternary carbon and an electronegative atom (oxygen) respectively at the two ends, characteristic of the lactonic *Gentiana* alkaloids. The proton (broad singlet) at 8·10 ppm may be assigned to a deshielded olefinic proton. The other two protons being labile could be replaced by deuterium. Gentiocrucine has a double bond. The presence of two hydrogen atoms exchangeable by deuterium has been confirmed by mass spectrometry. The presence of a primary amide group is revealed by its hydrolysis with HCl resulting in the formation of ammonium chloride.

Gentiocrucine contains a carboxylic group and a double bond at the sites of the methyl and hydroxyl group of mevalonic lactone. Since oxidation of a methyl group to a carboxyl group, and elimination of a hydroxyl group as water, are both biochemically possible, a biogenetic relationship between these compounds may be discerned [*Chemy Ind.*, (1969), 49].

New methods to destroy disease carrying organisms

Two new developments have been reported to kill disease spreading organisms that live in water or are carried by water. One of the methods, patented by the US company, B. F. Goodrich Co., uses toxic substances compounded in rubber; in the other method developed at the Northwestern University, USA, gamma radiations from cobalt-60 are used to destroy the organisms.

In the first method, a toxicant, like an organotin compound or an alkanolamine salt of salicylanilide, in the form of powder or oil, is dissolved in a vulcanizable rubber matrix. The resulting vulcanized composition is cut into the most desired form — pellets, pieces, tapes, or sheets — and immersed in water containing the organisms.

Due to their low solubility, the toxicants are released into the water over a period (about one year) at a slow and controlled rate, so that concentrations harmful to fish or cattle are not built up. During the period of solubility, the rubber matrix holds the toxicant in water. Though neoprene rubber is preferred, others like nitrile, butyl-, and styrene-butadiene rubbers can also be used. The release rates and the resulting concentrations of the toxicants can be controlled by processing.

In field tests, the method has been used to destroy water-living larvae of mosquitoes, flies, midges and their hosts. These organisms are responsible for transmitting malaria, yellow fever, dengue fever and other diseases.

Due to the low cost of production and the safe and effective application even by unskilled persons, the method may be advantageous in the developing countries.

At the Northwestern University Puerto Rican snails (*Australorbis glabratus*), carriers of the snails fever, have been exposed to cobalt-60 gamma radiation of 75-250 kilorads/hr dose. Within half an hour all showed radiation injury and after 1 hr exposure all died following exposure.

Though large-scale adoption of the method awaits the development of practical means of irradiating the snails, one suggestion is to embed cobalt-60 capsules in shielded pipes carrying irrigation waters [*Chem. Engng News*, **47** (2), (1969), 38].

Department of Atomic Energy, India

The report of the Department of Atomic Energy (DAE), India, for the period 1967-68 records significant advances in research in its various constituent units.

Bhabha Atomic Research Centre (BARC) — All the three reactors — Apsara, CIRUS and Zerlina — were fully utilized for research. The Nuclear Physics Division had, among other notable achievements to its credit, the employment of a high resolution lithium-drifted-silicon detector with a field-effect transistor, to detect the X-rays. This set-up is also potentially useful for the non-destructive identification of the elements in any material. Another important work of this Division was the use of thermal neutron beams from the CIRUS reactor, in studies on solid, liquid and gaseous media employing a variety of techniques. Complete three-dimensional neutron data collected on a single crystal of beryllium sulphate tetrahydrate were analysed to give its complete structure without recourse to any X-ray information. A fully automatic 3-dimensional diffractometer was completed.

The Electronics Division fabricated several instruments/systems for use both at home and for export.

The Atomic Fuels Division was concerned with the production of the fuel elements and certain components required for CIRUS and Zerlina in particular, and for the country's nuclear power programme in general. The Division succeeded in producing very high density pellets possessing relatively fine grain size.

In the Chemistry Division, extremely pure metals like antimony,

bismuth, tellurium, silver, gold and also several compounds of tantalum, etc., were prepared. A large electrolytic cell for the recovery of gallium from Bayer liquor was fabricated. This development is of immense help to the aluminium industry. The Radiation Chemistry Section achieved a large measure of success with silver oak and vellapine in the investigations towards the production of wood polymers. The design details of the gas liquid chromatograph were released through the National Research Development Corporation to a private company for large-scale production. Each instrument would save about Rs 10,000 in foreign exchange and the assessed demand in the country is about 100 instruments per year.

The Isotope Division produced radioisotopes of the approximate value of Rs 1·3 lakhs for export. For the first time, a 1800-curie cobalt-60 source for deep cancer therapy was supplied to a hospital. Another noteworthy contribution of this Division was the fabrication and installation at the Central Mechanical Engineering Research Institute, Durgapur, of a remotely operated 20-curie cobalt-60 radiography camera.

During the year, BARC organized a summer school on 'Switching theory and automata theory', a summer school on 'Solid state physics'; and a winter school in 'Molecular biology'.

Tata Institute of Fundamental Research (TIFR) — In the School of Physics at the TIFR, the principal research activities in theoretical physics related to particle physics, nuclear physics, solid state physics, magnetohydrodynamics and astrophysics. The effect of the addition of impurity in solids, liquids and gases on the long-lined component of positronium was studied; this provided useful information about pair correlation and the Fermi surface in various metals.

The CDC 3600-160A computer system of the National Computational Centre completed its third year of operation in October 1967. About 60 scientific and engineering research and educational organizations, government and private sector agencies used this facility during the year. A prototype on-line console was designed and this has enabled the development of a time-sharing system.

In the field of computer and operations research, a very flexible speech synthesis package for the CDC 3600 computer system, called SPEECH, was developed. It accepts typewritten input in phonetic alphabet from the console, synthesizes the specified speech fragment, and plays it back. While conversational utterances in several languages have already been synthesized, attempts to incorporate prosodic features in the output speech are under way. Audition experiments were also done to test the psychological aspects of the synthesized speech.

In the area of nuclear structure physics, a study of stripping reactions at low deuteron energies was undertaken using the cascade generator; the Coulomb field plays an important role in these reactions, and spectroscopic factors could be determined from such stripping experiments. Use was made of the cascade generator to study the fission of uranium-238 and thorium-232.

Analysis of data collected at Ootacamund for the study of extensive air shower array was completed. It was observed that in high energy collisions, appreciable production of nucleon-antinucleon pairs occurs and that there is a broadening of the lateral distribution of high energy nuclear active particles.

A new facility is being set up for the large-scale processing of photographs taken with bubble chambers. It would now be possible for India to actively participate in global pursuit of knowledge in this field, at a moderate cost.

In the field of oceanography, the discovery of marked disequilibrium in the ratio $^{234}Th/^{238}U$ in surface marine waters up to 100 m depth has opened up new possibilities of studying rapid geochemical reactions near the surface. Measurements of radon content in the surface over the Arabian Sea have been extended.

In radio astronomy, the design of the large cylindrical telescope (to be installed at Ootacamund) has been completed. It is noteworthy that all the electronic components needed for this telescope have been designed and built at TIFR.

In the field of solid state electronics, fabrication of simple semiconductor devices was undertaken and about 1000 planar switching transistors have already been fabricated.

A significant observation made in molecular biology was that the uptake of DNA is confined only to the competent cells and that the cells having a simple nucleus are most likely to be capable of transformation. Evidence was obtained to indicate that the pairing of donor DNA does not occur simultaneously with its transfer.

Physical Research Laboratory (PRL), Ahmedabad — Investigations on cosmic rays and associated astrophysics studies were continued. A super neutron monitor was built for continuous monitoring of the cosmic ray intensity at Ahmedabad. Regular vertical soundings of the ionosphere were made from Thumba and Ahmedabad during the year.

Saha Institute of Nuclear Physics — Research in nuclear chemistry progressed considerably at the Saha Institute of Nuclear Physics, Calcutta. An improved method of measuring low level activity and techniques for the recovery of the products of spontaneous fission have been developed. Systems for working out chemical analysis through neutron activation have been devised. A procedure for recovering tracer amounts of caesium from molasses of Indian origin has been successfully worked out. A new method for determining the transition temperature with radioactive isotopes has been developed by the study of mixed crystal formation. A 3 kW induction heating machine, an X-ray machine and a Debye-Scherer powder camera have been successfully fabricated at the Institute.

Tata Memorial Hospital and the Indian Cancer Research Centre were amalgamated into one body, called the Tata Memorial Centre, under a Council. The aims of the Centre are: to conduct intensive research directed towards the advancement of knowledge in the field of cancer, to combat cancer in all its forms by care and study of patients, and to provide education and training to physicians and investigators in special fields.

Space research — Two Judi-Dart meteorological rockets were launched at the Thumba Equatorial Rocket Launching Station (TERLS). The Dart system of payload was developed by TERLS. The experiments were successful and wind data in the region 60-70 km were obtained. A Space Science and Technology Centre (SSTC) has been set up on Veli Hill by the side of TERLS. Its major responsibility is to develop sounding rockets of superior performance, expertise in aerospace engineering as well as in ground-based experiments, and scientific payload construction. Under the Rocket Development Programme at the SSTC (Project Rohini), eight Rohini-RH 75 rockets, fabricated indigenously, were flight-tested from the Thumba range for systems check. The performance of these rockets was satisfactory.

The exploratory drilling operations by the Atomic Minerals Division revealed new promising occurrences of uranium in Bihar. A radioactive carbonaceous-clay horizon immediately overlying the lignite bed, about 55 m below the surface, exposed in Neyveli Lignite Mine on recent systematic sampling showed significant uranium values.

The Indian Rare Earths Ltd earned foreign exchange of over a crore of rupees during 1966-67; it won the ICMA (Indian Chemical Manufacturers Association) award for outstanding performance in export promotion for exports of a product of the chemical industry.

The Electronics Corporation of India Ltd was formed with its registered office in Hyderabad. Its main function is the production on a commercial scale of a variety of nuclear instruments, control panels, electronic components, etc. Another corporate body, the Uranium Corporation of India Ltd, was formed and is located at Jaduguda. Its main responsibility is the development of the uranium mine and the operation of the uranium mill at Jaduguda.

Apart from the above-mentioned activities, the Department gave financial assistance to the extent of Rs 12·35 lakhs to various universities and institutions for work on specific research projects related to nuclear sciences.

FORTHCOMING INTERNATIONAL SCIENTIFIC CONFERENCES, 1969

Date	*Conference*	*Place*
9-15 Sept.	Thirty-sixth International Foundry Congress	Belgrade
14 20 Sept.	International Symposium on Germ-free Animal as a Tool in Research	Belgium
15-19 Sept.	International Industrial Conference	San Francisco
15-20 Sept.	Third International Congress of Chemical Engineering, Chemical Equipment and Automation	Marianske Lazne
17-24 Sept.	International Cyclotron Conference	Oxford
22-23 Sept.	International Conference on the Use of Cyclotrons in Chemistry, Metallurgy and Biology	Oxford
22-24 Sept.	Seventh International Conference on Condensation and Ice Nuclei	Prague
23-26 Sept.	Fourth International Powder Metallurgy Conference	Dresden
24-26 Sept.	Third International Micrographic Congress	Frankfurt
24-27 Sept.	Second International Congress on the Theory of Machines and Mechanisms	Zakopane
24-27 Sept.	International Conference on Amorphous and Liquid Semiconductors	Cambridge
30 Sept.-2 Oct.	Fourth International Synthetic Rubber Symposium and Exhibition	London
September	International Symposium on Analytical Chemistry	Birmingham
6-8 Oct.	International Electronics Conference and Exposition	Toronto
6-9 Oct.	Second International Committee for the Study of Bauxites, Oxides and Hydroxides of Aluminium	Budapest
6-11 Oct.	Second International Nuclear Industries Fair and Technical Meetings	Basel
6-11 Oct.	Second International Congress for Project Planning	Amsterdam
6-11 Oct.	Twelfth International Congress of Radiology	Tokyo
7-10 Oct.	Fifth International Conference on Separation Methods: Column Chromatography	Lausanne
21-24 Oct.	First International Conference on Quality Control	Tokyo
27-29 Oct.	Ninth Interscience Conference on Antimicrobial Agents and Chromatography	Washington

Announcement

▪ *A Symposium on Low Cost Waste Treatment* is being organized by the Central Public Health Engineernig Research Institute, Nagpur, during 27-29 October 1969. Following the opening session on 27 October, there will be seven technical sessions devoted to the following topics: (I) (1) Some theoretical aspects of extended aeration process; (2) Types of oxidation ditches and their performance; (II) (1) Design of oxidation ditches; (2) Design of rotor and its oxygenation capacity; (3) Excess sludge, its withdrawal and drying; (4) Problems in operation of oxidation ditches; (III) (1) Use of package plants for sewage treatment; (2) Examples of oxidation ditches in India; (3) Tertiary treatment with oxidation ditches; (IV) (1) Aerated lagoons and their performance; (2) Design and construction of aerated lagoons; (V) (1) DOC/BOD relationships for sewage and industrial wastes; (2) Cost analysis for different waste treatment methods; (VI) (1) Anaerobic lagoons in waste treatment; (2) Performance studies on oxidation ponds in India; and (VII) (1) Die-away of pathogens in sewage treatment; (2) Miscellaneous methods (septic tanks, etc.)

Further details regarding the symposium can be had from the Director, Central Public Health Engineering Research Institute, Nagpur.

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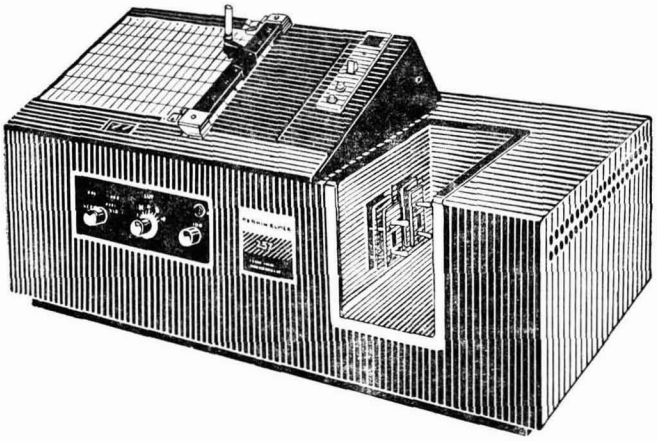

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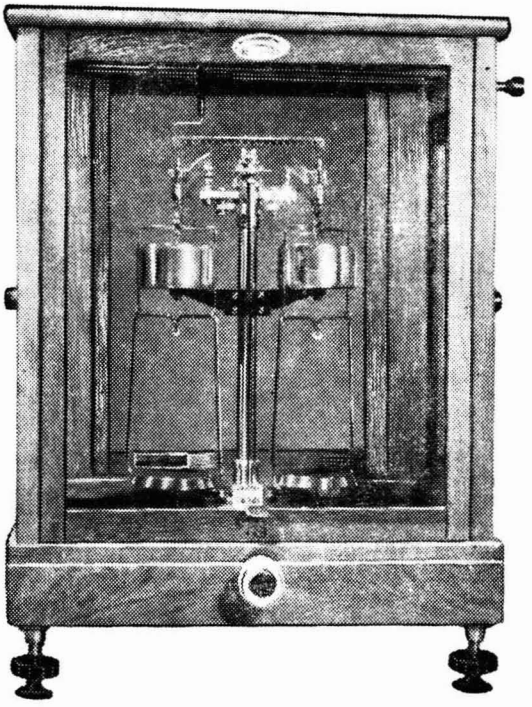

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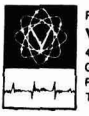

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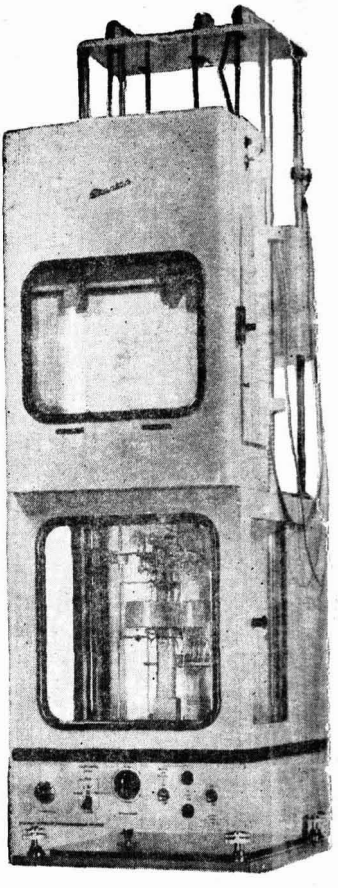

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