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# THE RHEOLOGY LEAFLET



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No. 6

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## THE RHEOLOGY LEAFLET

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## ONCE MORE

Remember the meeting of the Society of Rheology, Christmas week at Pittsburgh. Full details and program will appear in the next issue of the Rheology Leaflet.

The local committee is:

Dr. E. Ward Tillotson, Chairman  
Mellon Institute, Pittsburgh

Dr. A. Nadai, Dr. E. Hutchisson, Dr. R. G. Sturm.

The program committee is:

Mr. H. R. Lillie, Chairman  
Research Division, Corning Glass Works, Corning, N. Y.

Prof. E. C. Bingham, Dr. M. B. Hersey, Dr. H. F. Wakefield,  
Mr. R. N. Traxler, Prof. E. Hutchisson.

Send in the title and a 100 word abstract of your paper to H. R. Lillie at once, and plan to attend the meeting.

## WE WANT TO KNOW

How do you like the Rheology Leaflet? Please write the Secretary of the Society,

R. L. Peek, Jr.  
Sec'y Society of Rheology  
Bell Telephone Laboratories, Inc.  
463 West St., New York, N. Y.

telling him specifically what you like and what you don't like about the Leaflet. Your officers want to have the Leaflet fill your needs. We can do this best if you let us know what you want most. Specifically, do you want more news or less, more abstracts or fewer, longer abstracts or shorter, extensive abstracts of papers given at our annual meetings which happen not to be of the strictly research type ordinarily found in journals like Journal of Applied Physics? Be sure to let us know, so that we can help you most. If we don't hear from you we have to assume that you are completely satisfied. Are you?

## NEWS OF RHEOLOGY AND OF RHEOLOGISTS

On July 4th and 5th the Institute of Physics (London) held a conference on elasticity and plasticity at the University of Manchester. The conference was given the active support of the Plastics Group of the Society of Chemical Industry. Authors of papers included Prof. G. I. Taylor, Dr. R. W. Bailey, Prof. E. N. Andrade, Dr. F. T. Peirce, Dr. J. B. Speakman, and Dr. W. G. Wearmouth.

We are glad to record that Dr. M. B. Hersey's book "Theory of Lubrication" (John Wiley and Sons) is now in its second printing. The new issue has 180 pages, and has not only 100 new references, but also a brief additional section on "recent developments".

The American Society for Testing Materials has published the papers given at its symposium on "plastics".

The Industrial and Engineering Chemistry division of the American Chemical Society will hold a symposium on Fluid Dynamics in Pittsburgh at the time of the Society of Rheology meeting. All rheologists should attend this joint session.

The papers presented during the Symposium on Consistency at the meeting of the American Society for Testing Materials held in New York City June 29, 1937 have been made available in booklet form. The publication may be obtained from A.S.T.M. Headquarters, 260 South Broad Street, Philadelphia, Pennsylvania, at 85 cents a copy. The contents include:

Introduction—W. H. Fulweiler.

Recent Progress in Consistency Measurement—Eugene C. Bingham.

Definition of Consistency and Theoretical Considerations—M. Mooney.

Consistency Measurements in the Paint Industry—D. L. Gamble.

The Flow Properties of Asphalts Measured in Absolute Units—R. N. Traxler.

Consistency Measurements in the Coal Tar Industry—E. O. Rhodes, E. W. Volkmann and C. T. Barker.

Viscosity Measurement of Petroleum Products and Lubricants—J. C. Geniesse.

Consistency Measurement of Rubber and Rubber Compounds—J. H. Dillon and L. V. Cooper.

Measurements of Flow Characteristics of Plastics—H. L. Bender, H. F. Wakefield and H. E. Riley.

Cold Flow of Insulating Materials—Robert Burns and Irving L. Hopkins.

The Fifteenth Colloid Symposium was held at the Massachusetts Institute of Technology, June 9th to 11th. Among the papers containing matter of interest to the rheologist were:

"Studies in Colloidal Clays", D. S. leBeau and E. A. Hauser.

"The Viscosity Characteristics of Clays", G. S. Broughton and B. S. Hand.

"Studies on Gelatin and the Production of Self-supporting Films from Colloidal Clays", E. A. Hauser and D. S. leBeau.

"The Dispersion of Proteins in Aqueous Formaldehyde Solutions", A. K. Smith, H. J. Max and Philip Handler.

"Further Investigation of the Chain Structure of High Molecular Structure", C. S. Fuller and C. J. Frosch.

"The Viscosity of Cellulose in Phosphoric Acid Solutions", A. J. Stamm and W. E. Cohen.

Viscosities of Unimolecular Films of Long Chain Alcohols", Lyman Fourt and W. D. Harkins.

"The Viscosity of Dilute Solutions of Long Chain Molecules" M. L. Huggins.

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The General Discussion on Lubrication and Lubricants, organized by the Institution of Mechanical Engineers and held in October, 1937, has been published in two volumes by the Institution. Many of the contributions are of rheological interest, among them:

"Relationship of the Pressure-Viscosity Effect to Bearing Performances", L. J. Bradford and C. G. Vandegriff.

"Influence of Pressure on Film Viscosity in Heavily Loaded Bearings", S. J. Needs.

"A Re-examination of the Hydrodynamic Theory of Bearing Lubrication", L. Prandtl.

"The Earlier History of the Hydrodynamic Theory of Lubrication Friction", A. Sommerfeld.

"Oil Viscosity in Relation to Cylinder Wear", C. G. Williams.

"Molecular Forces in Friction and Boundary Lubrication", N. K. Adam.

"The Flow Characteristics of Petroleum Lubricants", D. P. Barnard.

"The Determination of the Viscosity of Oils at High Temperatures". Guy Burr.

"The Influence of Increase of Temperature, of Oiliness and of Surface Conditions on Viscosity", H. Brillie.

"Viscometry as Applied to Petroleum Products in the United States". J. C. Geniesse.

"Graphical Solutions of Viscosity Problems", J. Groff.

"Physical Properties of Lubricants", Yoshio Suge.

"The Relations Between the Chemical Constitution and the Properties of Lubricants", Dr. Zorn.

"The Problem of Oiliness", S. Kyropoulos.

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American Society for Testing Materials, Tentative Standards, 1937, covers many tests involving deformation such as compressive strengths of cements and ceramic materials, viscosities of petroleum products, rubber, both vulcanized and in solution, and definitions of terms relating to rheological properties of matter.

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Annual Tables of Constants, No. 5, Published by McGraw-Hill Book Co., Inc., is edited by Koch, Sture, Taylor, T. W. J., Auger, P., and Dervichian, D. G., covers Elasticity, Compressibility, Expansion, Density, Viscosity and Surface Tension.

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### The Eyring Theory of Viscosity and Plasticity

Any theory which gives a mechanical picture of the underlying causes of viscosity and plasticity is, in the very nature of things, of inherent interest to rheologists. When such a theory predicts experimental results with reasonable accuracy it becomes not only interesting but useful. It is for this reason that we give in this issue a summary of three papers by Henry Eyring of Princeton University in the Journal of Chemical Physics; **4**, 283, (1936), **5**, 726, (1937), and **6**, 391, (1938).

By considering viscous flow as a chemical reaction in which the elementary process is the passing of a single molecule from one equilibrium position to another over a potential barrier, Eyring has developed the general equation:

$$\eta = \frac{\lambda_1 h}{\kappa \lambda^2 \lambda_2 \lambda_3} \cdot \frac{F_n}{F_a^*} \exp \frac{\Delta E_{act}}{\kappa T}$$

where  $\lambda$  = distance between equilibrium positions in the direction of flow,

$\lambda_1$  = perpendicular distance between adjacent layers of molecules.

$\lambda_2$  = distance between adjacent molecules in the direction of flow.

$\lambda_3$  = distance between molecules in the plane of flow and normal to the direction of flow.

$\kappa$  = transmission coefficient.

$F_n$  = partition function of normal molecule.

$F_a^*$  = partition function of activated molecule, omitting the degree of freedom corresponding to flow.

$\Delta E_{act}$  = activation energy for the flow process; assumed to be some fraction,  $1/n$ , of the energy of evaporation. For spherical molecules,  $n=3$ , while for non-spherical molecules,  $n$  lies between 3 and 4.

Since  $K$  is usually unity for chemical reactions, Eyring assumes that it is unity in his discussion of viscosity, plasticity, etc. This equation reduces to a number of the successful empirical equations under the appropriate limiting conditions. The increase of viscosity with shearing stress is explained. The theory yields an equation for the diffusion coefficient which, when combined with the viscosity gives a satisfactory and suggestive interpretation of diffusion of molecules of about the same size. Under such conditions, apparently Eyring's theory should replace the usual theories for diffusion coefficients and for absolute electrical conductance.

It is shown that the ratio

$$\frac{\Delta E_{vap}}{\Delta E_{vis}}, \text{ where } \Delta E_{vis} = R d \ln \eta/d(1/T),$$

can be taken as an index of the size and shape of the molecule, or, more precisely, of the unit of flow in the liquid. The activation energy for flow in liquid metals is a very small fraction of the energy of vaporization, ranging from  $1/10$  to  $1/25$ , leading to the conclusion that the metal ions flow without their valence electrons. Viscosity data confirm the  $S_8$  ring structure for sulfur below  $160^\circ$ , and lead to the conclusion that above  $250^\circ$  sulfur probably consists of long chains containing as a rough average about 36 sulfur atoms. In the long chain hydrocarbons, the activated configuration for flow is probably a curled-up molecule. The structure activation energy of flow in associated liquids due to the hydrogen bond structure is discussed, and viscosity data are used to compute the degree of coordination in liquid water. At high pressures the energy of vaporization in the equation must be replaced by  $V$  ( $P$  internal. +  $P$  external). This yields an equation for computing the viscosity of liquid under pressure. Finally, the equation for the fluidity of a liquid is modified to interpret the viscosity data for liquid films. Equations are given for the pressure and temperature effect on surface viscosity, and a knowledge of these effects is used to interpret the structure of the films. These three papers are well worth serious study by all who are interested in the underlying theory of flow.

## ABSTRACTS AND BIBLIOGRAPHIES

Collected by H. F. Wakefield

**Effect of pressure upon the Elastic Parameters of Isotropic Solids, according to Murnaghan's theory of Finite Strain.** F. Birch J. Applied Phys. 9, 279-88 (1938).—Murnaghan's theory of finite deformations is applied to a hydrostatic pressure upon the elastic coefficients of an isotropic body, for small strains superposed on the hydrostatic strain.

**Viscosity of Oil-Water Emulsions.** G. Broughton and A. L. Squires. J. Phys. Chem. 42, 253-63 (1938).—The viscosity of a concentrated emulsion is a function of the rate of shear approaching an asymptote as the rate of shear is increased. Over wide ranges the relation between shearing stress and the rate of shear is linear. Other than volumetric concentration, the type of stabilizer employed seems to be the variable of most significance in determining the magnitude of the viscosity of any phase pair. Stabilizers producing the best emulsification give emulsions of the lowest limiting relative viscosity.

**Agglomeration and viscosity in dilute suspensions.** G. Broughton and C. S. Windebank. Ind. Eng. Chem. 30, 407-9 (1938).—Expts. at 25° with suspensions of spherical particles of glass and kaolin in an inert org. liquid of equal d., "in which marked agglomeration of particles was observable, indicate that the Einstein relation holds only for spheres of relatively large size (50-200 $\mu$ ) at low concns." It is not clear why smaller spherical particles (3-12 $\mu$ ) give rise to a viscosity higher than the Einstein value by a percentage independent of concn. Suspensions of mica particles, 65-100 mesh and 100-200 mesh, "diverge widely from the Einstein relation even at low concns. and show yield points at concns. far lower than spherical particles of comparable size."

**The reaction rate theory of viscosity and some of its applications.** J. Appl. Physics. 9, 252-69 (1938). R. H. Elwell.—The theory of potential energy barriers of reaction rates is applied to flow of plastic materials on the assumption that the retardation effect is passage over a potential barrier. Flow is considered as a unimolecular process of a molecule passing from one equilibrium position to another. Problems of viscosity, plasticity and diffusion in liquids, glasses and resins are thus treated by reaction rate equations. A relationship between viscosity and vapor pressure is stressed and the theory is compared with some well-known empirical equations. Flow is considered by vaporization with one degree of freedom and involves breaking both undirected forces (van der Waals, dipole) and directed

or structural forces. The relative importance of these two groups of forces differ in the different liquids.

**Theory of plastic deformations and twinning.** J. Frankel and T. Kontorowa. *Physik 2. Sowjetunion.* 13, 1. 1-10 (1938).—An elementary scheme of the process of plastic deformation or twinning is proposed consisting of a caterpillar-like motion of one atomic chain over another which is supposed to remain fixed.

**Measurement of thixotropy in absolute units.** *Trans. Faraday Soc.* 34, 511-20 (1938). C. F. Goodeve and G. W. Whitfield.—It has been shown that a kinetic treatment of thixotropy leads to a method of measurement involving a steady state in which the spontaneous growth of internal structure is compensated by a break-down process arising from a steady applied shear. The resistance to flow in the steady state is governed by two parameters, a coefficient of thixotropy and a coefficient for the residual viscosity. Measurements made on carbon black suspensions using a new type of apparatus, together with measurements made by previous observers, are shown to be in conformity with the theory.

**Mercury Dynamics I. Theory of the Laminar flow of an electrically conductive liquid in a homogeneous magnetic field.** Jul. Hartman *Kgl. Danske Videnskab Selskab. Math-fys. Medd.* 15, No. 6, 28 pp (1937) (in English).

**II. Experimental investigations of the flow of mercury in a homogeneous magnetic field.** Jul. Hartman and Freimut Lazarus *Ibid.* No. 7, 45 pp. (in English).—The effect of high intensity magnetic fields upon laminar and turbulent flow.

**Solution of the Laminar Boundary Layer Equations.** L. Howarth. *Roy. Soc.* 164A, 547-79 Feb. 15 (1938).—The problem of the flow along a flat plate placed edgewise to a steady stream, when a retarding pressure gradient varying linearly as the distance  $X$  from the leading edge of the plate is superposed, is discussed. The problem is reduced to the solution of a first order differential equation.

**Theory of crystal plasticity.** Albert Kochendorfer. *Z. Physik* 108, 244-64 (1938).—A theory of crystal plasticity is developed, based on the following: At the boundaries of the ideal mosaic block, of which the classical crystal consists, displacements are produced because of the existing inhomogeneous strains. The threshold energy in pure thermal formation is approx. 50,000 cal. for  $N$   $6.06 \times 10^{23}$ . A displacement wanders under the influence of the outer tension

through the mosaic block. This wanders to the boundaries and is held there until released by the thermal vibrations and inhomogeneities in tension. Equations are derived, and it is shown that the displacements result in the formation of an inner field of tension which opposes the outer field. The equations for gliding velocity are discussed.

**Stream Flow.** G. Nebbia. *Accad. Lincei, Atti*, 26. pp. 433-439, Dec. 19, 1937.—The conception of the "total quantity of motion in stream flow is applied to a number of cases of free flow with gradual change, but the results can be applied to problems involving a sudden change of flow.

**Motion of an Elliptic Cylinder in a Converging Stream.** S. Oka. *Phys. Math. Soc., Japan, Proc.* 20, pp. 105-109, Feb. 1938. In English.—The two-dimensional motion of an elliptic cylinder in a converging stream of incompressible, perfect fluid, whose velocity potential is given by  $\phi_0 = -U_0 x + C(y^2 - x^2)/2$  is discussed. Expressions are derived for the velocity potential of the motion round the cylinder, the pressure at any point in the fluid and the resultant moment about the centre of the ellipse. The equilibrium of a very flat elliptic cylinder in the stream is discussed.

**Efflux Phenomena Occurring at Sharp-Edged Orifices.** D. Pavel, *Bull. Math. et Physique*, 8. 1-3. pp. 158-167, 1936-1937. In German.—The efflux of water through orifices of various forms viz., triangular, rectangular, star- and slit-shaped orifices, is discussed theoretically and studied experimentally. Measurements are made of the coefficient of contraction, the resistance coefficient, the change of shape of the jet along its length, and the distribution of velocities in a cross section of a jet.

**Molecular Processes at the Elastic Limits.** A. Smekal. *Physik Z.* 39, 228-30 (1938).—A review.

**Molecular Weight and Viscosity of Polymers.** H. Staudinger. *Kolloid Zeits.* 82, 129-31 (1938).—This paper is supplementary to, and critical of, Dobry's recent publications on the osmotic and viscosimetric data afforded by cellulose derivatives and polystyrene. The present author finds that by chemical investigations such as the transformation of polymeric substances into analogous polymerized products, it may be decided whether the colloidal particles form macromolecules or micelles; moreover, the magnitude of the macromolecules may be determined from osmotic data and their shape deduced by viscosimetric experiments. In the case of fibre molecules, their molecular magnitude may be determined from viscosity data.

**Distribution of Velocity in Turbulent Flow.** J. J. Sommer. *Physik. Z.* 39, 110-27 (1938).—This paper contains an attempt to use the ideas of the kinetic theory of gases to describe turbulent flow.

**Force on an Elliptic Cylinder Moving in a Liquid Endowed with Uniform Vorticity.** Y. Tasiro. *Phys. Math. Soc., Japan, Proc.* 20, pp. 91-99, Feb., 1938. In English.—The undisturbed motion of a uniform incompressible inviscid fluid being represented, relative to fixed axes by  $u = -2\omega By$ ,  $v = 2\omega Ax$  (with  $A + B = 1$ ) so that the vorticity is constant, the author finds formulae for the force and moment on an elliptic cylinder at any orientation relative to the fixed axes and moving in any manner through the fluid.

**Supersonic Measurement of Elastic Constants of Solids.** A. Walti. *Helv. Phys. Acta*, 11, 2, pp. 113-139, 1938. In German.—A previous paper by R. Bar and A. Walti describes the principle of a method of determining the elastic constants of isotropic solids. In order to determine the elastic constants of the body the wave-length of compression and transverse waves of known frequency must be known. In the present paper an improved experimental arrangement is described by means of which the transmission maxima through a sheet of glass are determined for perpendicular and oblique incidence in the frequency range  $10^6 - 10^7$  cycles. From these measurements the wave-length of compression and longitudinal waves is deduced by means of a theory of H. Reissner. The values of these velocities are independent of the angle of incidence and the thickness of the sheet; the elastic coefficients deduced, namely, Poisson's ratio, Young's modulus and the torsion modulus, agree within the limits of error with the usual static values.

**The influence of the temperature and the specific volume on the viscosity of liquids.** W. R. van Wijk and W. A. Seeder. *Physica* 4, 1073-88 (1937) (in English).—Exptl. formulas for the relation between viscosity and temp. are divided into those in which temp. is assumed to be only indirectly responsible for the change in viscosity, through the expansion of the liquid, and those in which temp. is assumed to exercise a direct effect by activating the mols.

**Constitution and Viscosity Association of High-Molecular Hydrocarbons.** B. Yamaguchi. *Chem. Soc., Japan, Bull.* 13, pp. 61-77, Jan., 1938. In English.—The viscosity of solutions of four oils in benzene was determined, and an empirical equation connecting the viscosity association and the temperature coefficient of viscosity was derived. The viscosity association and temperature coefficient of viscosity of solutions of three polystyrenes differing markedly in polymerization

were also determined. The same empirical relationship holds for these solutions as for the oils. The effect of constitution on the viscosity association of high-molecular hydrocarbons was examined, the effect of length of side chain, straight chain as compared with branched chain, ring structure and olefinic linkages in the side chain being determined.

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