

RHEOLOGY BULLETIN



πάντα ῥεῖ

Publication
of the
SOCIETY OF RHEOLOGY

Vol. XIII No. 1

February 1942

RHEOLOGY BULLETIN

Published Quarterly by

THE SOCIETY OF RHEOLOGY

Dedicated to the Development of the Science of the
Deformation and Flow of Matter

175 Fifth Avenue

New York, N. Y.

THE SOCIETY OF RHEOLOGY IS ONE OF THE
FIVE FOUNDER SOCIETIES OF THE
AMERICAN INSTITUTE OF PHYSICS

HERMAN MARK, President
Dept. of Chemistry
Polytechnic Institute of Brooklyn

W. F. FAIR, JR., First Vice-President
Mellon Institute of Industrial
Research
Pittsburgh, Pennsylvania

P. J. FLORY, Second Vice-President
Esso Laboratories
Standard Oil Development Co.
Elizabeth, New Jersey

NELSON W. TAYLOR, Editor
Dept. of Ceramics
The Pennsylvania State College
State College, Pa.

H. F. WAKEFIELD, Publishing Editor
Bakelite Corporation
Bloomfield, New Jersey

R. B. DOW, Secretary-Treasurer
Ballistics Research Laboratory
Aberdeen Proving Ground, Maryland

Non-member Subscriptions: \$2.00 Annually

Single Copies: 75c

Address All Communications to the Editor

RHEOLOGY BULLETIN

Vol. XIII., No. 1

πάντα ῥεῖ

February, 1942

TABLE OF CONTENTS

	Page
Editorial—War and the Physicist	2
In Memoriam, Frederick H. Getman	2
The 1941 Fall Meeting	4
Symposium on Viscosity, Molecular Size and Molecular Shape	4
Plans for the 1942 Fall Meeting	5
Symposium on Consistency	5
The British Rheologists' Club	6
Viscosity Nomographs, Bibliography	8
Rheology Progress Abstracts	
Bituminous Materials	10
Glasses and Slags	10
Liquids and Solutions	15
Polymers	18
Resins	22
Rubber	23
Theory	24
Letters to the Editor	29

The November 1941 issue of RHEOLOGY BULLETIN which would have been No. 4 of Volume XII was not published. The national emergency and the state of the Society treasury seemed to make this omission advisable.

EDITORIAL

War, and the Physicist

Our country is now engaged in a life and death struggle with three powerful dictatorship nations whose methods and policies are brutal, treacherous and completely unscrupulous. In the all-out effort which every American citizen must make for victory, the physicist has a special responsibility, because his education and his experience and his unusual insight into the nature and properties of matter qualify him to provide new and better instrumental devices for the armed forces and for the production line. President James B. Conant, Chairman of the National Defense Research Committee says "This is a physicist's war rather than a chemist's. For the present at least, there appear to be more investigations of a physical nature than there are chemical military problems". In this connection an editorial "Selective Service and the Physicist", published in the Journal of Applied Physics, Vol. 13, No. 1, 1-2, January, 1942, is well worth study by every rheology worker who is trying to evaluate his own public obligations at this time.

Under the stress of war the Science of Rheology is being deformed in new directions and new ideas and facts are flowing forward with an accelerated velocity. Let the rheologist be plastic enough to absorb that which is good but elastic enough to recover quickly from the many shocks which will assail him. Let him meet the challenge of the hour with faith and fortitude, and may he work cooperatively with his fellow scientists for the common good. The Rheology Bulletin is the official medium of publication for the Society of Rheology. It is useful to rheologists in proportion to the support they give it by contributing abstracts of important scientific and technical articles, or other material of general interest. The Editor is just a "dollar-a-year man" with no ulterior motives, but with a lot of other duties and obligations. His task will be pleasant and his duties light if his readers cooperate by sending him in "all the news that's fit to print."

In Memoriam—Frederick H. Getman

Dr. Frederick Hutton Getman, Physical Chemist, died suddenly on December 2, 1941, at the Stamford Hospital in Stamford, Conn. He had been failing for several months but attended the meeting of the American Chemical Society in Atlantic City in September where he presented a paper.

He was born in Oswego, New York, on February 9, 1977. He was the son of Charles Henry and Alice (Peake) Getman. The family had a very considerable fortune, made in the lumber business, and young Getman had an assured position in business if he chose to follow his father's calling. However, his natural inclinations were along other lines. He early developed a taste for music, which remained with him throughout life. He was an excellent organist. Just when he decided to make science his major interest in life is not known to the writer, whether it was under Mallet or Remsen; but we have his own testimony of his love and admiration for the latter. He was educated at Rennsaeler Polytechnic Institute, Lehigh University, and the Department of Chemistry at the University of Virginia, from which he graduated in 1896. He was an instructor in chemistry and physics in the Stamford High School from 1897-1901. He then went to Johns Hopkins University where he received his Doctorate in Physical Chemistry in 1903. He was Fellow in Physical Chemistry at Johns Hopkins University from 1901-1903, but remained as Fellow by courtesy during the following year. He then became Carnegie Research Assistant for the year 1903-1904. Dr. Getman's first position after leaving Johns Hopkins was as lecturer in Physical Chemistry at the College of the City of New York. He was then lecturer at Columbia University in Physics from 1907-1908. He became Associate Professor in Chemistry at Bryn Mawr College in 1909 where he remained for six years.

The need for his counsel at Stamford in his father's business became so pressing that he then decided to change his base to Stamford, although continuing his scientific interests. He took an increasing responsibility in the Getman and Judd Company, of which he became Vice President. But at the same time he built and equipped the Hillside Laboratory of which he was a Director.

Dr. Getman's researches were begun with Dr. Henry C. Jones on the subject of "Hydration in Solution". They achieved notable results from their study of the freezing points of solutions. At Bryn Mawr Dr. Getman continued his work on solutions making a study of the viscosity of various solutions. At Stamford he installed refractometric and spectroscopic equipment for the study of solutions. Later work was devoted to electrode potentials and chemical activity. The titles of his various papers taken from CHEMICAL ABSTRACTS are much too numerous to give in detail.

Dr. Getman was author of several books of which two will be referred to here. His "Outlines of Physical Chemistry", of

late years in cooperation with Dr. Daniels, has gone through many editions and has been a standard textbook in American colleges for nearly a generation, excelling in clarity, conciseness, and scholarship. His "**Life of Remsen**" was published by the JOURNAL OF CHEMICAL EDUCATION as a pioneering effort in the publication of the lives of American chemists. Dr. Getman was engaged at the time of his death in securing the material for the publication of the lives of other American chemists. It is hoped that this work may be continued in other hands.

The broad interests of Dr. Getman are indicated by the fact that he was Director of the Stamford Hospital, the Stamford Trust Company, the Ferguson Library, and President of the Stamford Symphony Society. He was also active in the Presbyterian Church of Stamford. He married Miss Ellen M. Holbrook of Plymouth, Mass., on November 26, 1906, who survives him.

EUGENE C. BINGHAM

Report on the 1941 Fall Meeting

The 1941 Fall meeting of the Society of Rheology was held in connection with the meeting of the American Optical Society at the Hotel Pennsylvania in New York City on October 24-25, 1941.

The meeting had an attendance of about 75 persons, and was a very successful one. The papers given covered a wide range, and there was a lively discussion after practically every lecture. A number of new members joined the Society immediately after the meeting.

The elections held during the meeting had the following result: President, Herman Mark; First Vice-President, W. F. Fair, Jr.; Second Vice-President, P. J. Flory; Editor, N. W. Taylor; Publishing Editor, H. F. Wakefield; Secretary-Treasurer, R. B. Dow.

The present issue of the Bulletin is the first since the Annual Meeting. There was no November issue.

Symposium on Viscosity, Molecular Size, and Molecular Shape

A special symposium on "Viscosity" was held on February 2, 1942, at the Polytechnic Institute of Brooklyn, in connection with the TAPPI meeting of the Pulp and Paper Association. This symposium was attended by about 140 persons.

Dr. M. L. Huggins of the Eastman Kodak Research Department covered the present theoretical state of understanding of

the viscosity of pure liquids and solids, and Dr. M. A. Lauffer of the Rockefeller Institute for Medical Research gave a report on the present state of experimental methods and facts. Dr. W. O. Baker of the Bell Telephone Laboratories reported on recent measurements on the viscosity of high polymeric solutions. There was a lively discussion throughout the meeting. The speakers particularly emphasized the points in which our present ideas and methods have to be revised and improved. Abstracts of the first two papers are published in the present issue of the Bulletin.

It was a great satisfaction for the group that Dr. E. C. Bingham attended the meeting, thus showing that he had very successfully recovered from his illness.

Plans for the 1942 Meeting

The policy of the Society for the next years will be to improve and increase its fundamental knowledge of the laws of flow, to spread this knowledge amongst the groups and organizations which are interested, and to make it ready for practical application. Arrangements are now being made for two meetings of the Society of Rheology during the Fall of 1942. The first will be held during the September meeting of the American Chemical Society in Buffalo as a joint session with the Physical and Inorganic Division. This will be in the form of a Symposium on the Yield Value. In October we will hold a joint meeting with the Optical Society of America with much the same procedure as was followed in the Fall of 1941. Further announcements will be made in the next issue of the BULLETIN.

American Ceramic Society Symposium on Consistency

At the annual meeting of the American Ceramic Society, to be held in Cincinnati, April 19-26, the Refractories Division will conduct a Symposium on Plasticity, Consistency and Workability. This is a problem of major interest for those having to do with molding, pressing and casting of refractory clay shapes and furnace parts. The leader of the symposium is S. M. Swain, Director of Research, North American Refractories Company, Cleveland, O. The general program chairman of the Refractories Division is Mr. W. R. Kerr, Armstrong Cork Co., Beaver Falls, Pa.

Activities of the British Rheologists' Club

Bulletin No. 3 of the British Rheologists' Club, October 1941, issued by The Institute of Physics, The University, Reading, Berks, England, contains 40 abstracts of rheological interest, being serial numbers 49 to 88 inclusive. Titles, authors, and journal references are as follows.

49. Viscosities of homologous series at equal temperatures. A. H. Nissan and A. E. Dunstan. *J. Inst. Petroleum*, **27**, 222 (1941).
50. The viscosity of Russian and Rumanian lubricating oils at high pressure. R. B. Dow, J. S. McCartney and C. E. Fink. *J. Inst. Petroleum*, **27** 301 (1941).
51. The rheology of clay. H. H. Macey. *J. Sci. Instr.* **18**, 159 (1941).
52. High speed tension tests at elevated temperatures. A. Nadai and M. J. Manjoine. *J. App. Mech.* **8 A**, 77 (1941).
52. Colloid chemistry in ceramics. E. A. Hauser. *J. Amer. Ceram. Soc.* **24**, 179 (1941).
54. Fundamental study of clay: II. Mechanism of defloculation in the clay water system. A. L. Johnson and F. H. Norton. *J. Amer. Ceram. Soc.* **24**, 189 (1941).
55. Suspension media for float and sink concentration. Anon. *Mine Quarry*, **6**, 107 (1941).
56. Notes on the softening of coal. C. A. Seyler. *J. Inst. Fuel*. **14**, 195 (1941).
57. Non-ferrous physical metallurgy; present status of metal-thought on plastic deformation, strain hardening and recrystallization, copper-gas reactions, fatigue and magnesium alloys. R. M. Brick and A. Phillips. *Mining and Met.* **22**, 87 (1941).
59. The viscosity, protein distribution and gold number of the antenatal and postnatal secretions of the human mammary gland. H. Waller, R. Aschaffenburg and M. W. Grant. *Biochem. J.* **35**, 272 (1941).
58. Time and temperature effects in the formation of colloidal dispersions. P. G. Nutting. *J. Wash. Acad. Sci.* **31**, 41 (1941).
60. The determination of the viscosity of human milks and prenatal secretions. G. W. Scott Blair. *Biochem. J.* **35**, 627 (1941).
61. Variability in physical properties of Wisconsin butter. K. G. Weckel. *Nat. Butter and Cheese J.* **30**, 63 (1939).
62. Struktur der Butter und des Butterfettes. W. Mohr. *Molkerie Z.* **53**, 2335 (1939).

63. Emmental cheese body texture. G. Koestler. *Milchzeit.* 66, 83, 87, 93, 100. (1940).
64. Improvement in the viscosity of pasteurized cream, through subsequent heat treatment. H. F. Wiese, J. H. Nair and R. S. Fleming. *J. Dairy Res.* 22, 875 (1939).
65. Some factors affecting the body of market cream. F. M. Skelton and E. O. Herreid. *J. Dairy Res.* 24, 289 (1941)
66. Consistency of cheese curd at the pitching point and its bearing on the firmness and quality of the finished cheese. G. W. Scott Blair and F. M. V. Coppen. *J. Dairy Res.* 12, 44 (1941).
66. A preliminary study of the effects of varying pitching consistency and rate of scald on the physical and chemical properties of cheddar cheese and in the firmness of the cheese as judged by cheese-makers, bakers and others. G. W. Scott Blair, F. M. V. Coppen and D. V. Dearden. *ibid.* 170.
67. Speeds viscosity measurements in capillary type viscometer. E. H. Zeitfrichs. *Nat. Petrol. News.* 33 R, 121-R 124 (1941).
68. Mechanical properties of monolayers. S. Bresler, M. Judin and D. Talmud. *Acta Physicochimica U.S.S.R.* 14, 71-85 (1941).
69. Relation between rate of crystallization and viscosity of glasses. A. Leontjewa. *ibid.* 14, 245 (1941).
70. Plant waxes. L. Ivanovszki. *Oil and Colour Trade J.* 98, 944 (1940); 99, 98, 140, 174 (1941)
71. The flow properties of thermoplastics. I. W. G. Wearmouth and J. S. Small, *British Plastics*, 12, 377-9 (1941).
72. Plasticity of moulding compounds. R. Burns. *Modern Plastics.* 18, No. 9, 72-4, 104 (1941).
73. Supercooled silicates and their importance in considerations of the liquid state. E. Preston. *J. Phys. Sec.* 53, 568 (1941).
74. Elastic and thermoelastic properties of rubber-like materials. E. Guth and H. M. James. *Ind. Eng. Chem.* 33, 624 (1941).
75. Viscosity of chocolate. J. Stanley. *ibid.* Anal. Ed. 13, 398 (1941).
76. Structure and dynamics of liquids. W. E. Roseveare, R. E. Powell and H. Eyring. *J. Applied Phys.* 12, 669 (1941).
77. Correlation between elastic moduli and viscosities of liquids and plastics. A. Gemant. *ibid.* 12, 680 (1941).
78. Relaxation of metals at high temperatures. W. E. Trumper. *ibid.* 12, 248 (1941).

79. X-ray study of the changes which occur in aluminum during the process of fatiguing. R. G. Spencer and J. W. Marshall, *ibid.* **12**, 191 (1941).
80. Theory of the plastic properties of solids. F. Seitz and T. A. Read. *ibid.* **12**, 470, 538 (1941).
81. General theory of three-dimensional consolidation. M. A. Biot. *ibid.* **12**, 155 (1941). Consolidation settlement of a soil with impervious top surface. M. A. Biot and F. M. Clinigan. *ibid.* 578. Consolidation settlement under a rectangular load distribution. M. A. Biot. *ibid.* **12**, 426 (1941).
82. Frictional phenomena. A. Gemant. I. General. *ibid.* **12**, 530 (1941), II. A. Gases. *ibid.* **12**, 626 (1941).
83. Physical characteristics of synthetic rubbers. J. N. Street and J. H. Dillon. *ibid.* **12**, 45 (1941). X-ray study of the proportion of crystalline and amorphous components in stretched rubber. J. E. Field. *ibid.* **12**, 23 (1941).
84. Thermoplastic behaviour of linear and three-dimensional polymers. S. S. Kistler. *ibid.* **11**, 769 (1940).
85. Some relations of flow and physical properties with formulation in cellulose acetate plastics. W. E. Gloor. *ibid.* **12**, 420 (1941).
86. Physical aspects of boundary lubrication. O. Beeck. *ibid.* **12**, 512 (1941).
87. Photo-elasticity. Special photoelasticity number of J. Appl. Phys. **12**, 583-652 (1941).
88. The supply of physicists (including rheologists) in the U. S. A. Editorial. *ibid.* **12** 655 (1941).

Bibliography of Viscosity Nomographs

The following references are drawn from "A Bibliography of Chemical Engineering Nomographs," 84-page Document 1599, compiled by Roy Myllynen and D. S. Davis of Wayne University and filed with the American Documentation Institute, Science Service Building, 1719 N. Street, N. W., Washington, D. C. It is obtainable on microfilm for \$1.04 or in photocopies readable without optical aid for \$8.60. We are indebted to the "News Edition" of the American Chemical Society for this collection.

Alkalies

Davis, D. S., "Specific Gravity and Viscosity of Na_2CO_3 solution," *Chem. & Met. Eng.*, **47**, 690 (1940); "Viscosity Nomographs for Alkaline Solutions", *Ind. Eng. Chem.*, **28**, 953-56 (1936).

Cellulose

Davis, D. S., "Chart for Cuprammonium Viscosity of Rag Blends," *Paper Ind.*, **14**, 729 (1939); "Pulp Viscosity Nomographs," *Ibid.*, **17**, 101 (1935).

Womersley, J. R., "Fluidity Calculations for Cellulose Solutions," *J. Textile Inst.*, **26**; T165-70 (1935).

Conversion

Grosholtz, R., "Viscosity Conversion Charts from Temperature Relations," *Natl. Petroleum News*, **29**, 151 (Jan. 13, 1937).

Inst. Petroleum Tech. Viscosity Panel, "Viscosity Conversion over Range of Redwood Viscometer," *J. Inst. Petroleum Tech.*, **22**, 21-22 (1936).

Van Voorhis, M. G., "Viscosity Conversion Chart," *Natl. Petroleum News*, **27**, 32-34 (July 10, 1935).

Lubricants

Groff, Jean, "Nomograph for Lubricant Viscosity Variation with Temperature," *J. Soc. Ing. Automobile*, **11**, 200-10 (1938); "Nomograph for Viscosity-Temperature Relations for Lubricating Oils," *Ann. Soc. Belge Etude Petrole*, **3**, No. 12, 27-31 (1939).

Viscosity Index

Dean, E. W., Bauer, A. D., and Berglund, J. H., "Viscosity Index of Lubricating Oils," *Ind. Eng. Chem.*, **32**, 102 (1940).

Hersh, R. E., and Fenske, M. R., "Viscosity Index," *Oil & Gas J.*, **37**, 110 (May 19, 1938).

Newell, I. L., "Estimation of Viscosity Index of Oils," *Ind. Eng. Chem.*, **23**, 843 (1931).

Okhotkin, P. K., "Nomogram for Viscosity Index of Lubricants," *Neftyanoe Khoz.*, 1938, No. 1, 44-47.

Watson, K. M., "Viscosity Index at any Temperature," *Oil & Gas J.*, **33**, 34 (Aug. 2, 1934).

Miscellaneous

Barr, G., "Calculations of Equiviscous Temperatures of Tar," *Chemistry & Industry*, 1936, 576-77.

Davis, D. S., "Viscosity of Rosins," *Chemist-Analyst*, **22**, No. 4, 11 (1933); "Viscosity Nomograph for Salt Solutions," *Chem. & Met. Eng.*, **43**, 485 (1936); "Viscosity of Strong Phosphoric Acids," *Ibid.*, **47**, 155 (1940).

Genereaux, R. P., "Viscosity Data in Graphical Form," *Ind. Eng. Chem.*, **22**, 1382-90 (1930).

Grosholz, R., "Radical Charts Used to Supplement A. S. T.

M. Viscosity-Temperature Curves," Oil & Gas J., 33, 84-85, 87, 89 (March 28, 1935).

Nevitt, H. G., "Viscosities of Different Systems," Chem. & Met. Eng., 22, 1171 (1920).

Ubbelohde, L., "Nomograph for the Hagenbach Correction for the Hanging Level Viscometer," Oel Kohle Erdoel Teer, 11, 578-79, 611 (1935).

RHEOLOGY PROGRESS ABSTRACTS

Bituminous Materials

An interesting contribution to the literature of the rheological properties of asphalts has recently been made by Broome and Bilmes¹. They prepared strips of gunned asphalts which were then extended under constant stress and allowed to recover, thus obtaining strain/time curves for different stresses. From their experimental data they conclude that the gunned asphalt samples studied exhibited non-Newtonian flow and showed evidence of work-hardening. A model consisting of viscous and elastic elements is presented to aid in explaining qualitatively the flow properties of these asphalts, and agreement with an equation of Scott Blair and Coppen is announced. The authors also suggest that since "viscosity" cannot be used to describe the rheological properties of asphalts, the term "firmness" be used as defined.

The methods and suggestions offered in this paper are well worth considering during rheological investigations, but the writer believes that these proposals should not be adopted until the collection of similar data for the many kinds of asphalts of different sources, preparations, and histories, as well as for other bituminous materials, establishes whether or not such theories are of general application and validity.

Further explanation of the proposed definition of "firmness" is made by Scott Blair and Coppen² who list varied substances including bituminous materials in their discussion; this paper is of general interest to rheologists.

¹ J. Soc. Chem. Ind. 60, No. 7, 184 (1941).

² J. Soc. Chem. Ind, 60, No. 7, 190 (1941).

W. F. FAIR, JR.

GLASSES AND SLAGS

Elastic Aftereffects and Dielectric Absorption in Glass—Nelson W. Taylor. J. Applied Phys. 12, 753-58 (1941).

Taylor and Doran have found that in stabilized glasses the total elastic adjustment under a given load may be represented as the sum of several terms of the type $\lambda = \lambda_0 e^{-kt}$, and have drawn the conclusion that there are several sizes of complex sili-

cate ions in glass which respond independently and with different rates to applied stress.

Hopkinson proposed that there are several independent "elements" responding to the application of an electric field to a glass condenser, and von Schweidler showed that the anomalous charging current accompanying dielectric polarization is the sum of several terms of the type $i = Ae^{-t/\tau}$. This expression is identical in form with that for elastic polarization if the rate constant K is replaced by a characteristic relaxation time constant $1/T$. The dielectric phenomena thus appear to support the concept of independently acting ions in glass. This idea is in harmony with the X-ray evidence of a random ionic network, and with other physico-chemical evidence.

An interpretation of memory phenomena such as reversal effects in glass and rubber has been offered. Such reversals appear to be due to the superposition of two or more independent operations with different rate constants and directions.

The Viscosity of Slags and Glasses, Part I—A Discussion of the Methods of Measuring the Viscosity of Molten Silicates.—J. R. Rait, *Trans. Brit. Ceram. Soc.*, 40, (5), 157-204 (1941).

The literature of the methods of measuring the viscosity of molten silicates has been comprehensively reviewed. The measurement of viscosity of slags is essential to the iron and steel industries because it is an important factor for the correct working of the charge and for the study of corrosion on the refractory. Viscosity study is important to glass from the point of view of both its refining and working. The chief difficulties encountered in measuring the viscosity in molten glasses and slags were critically reviewed. All the fundamental methods of measuring the viscosity of liquids at high temperatures can be classified as follows: (1) Capillary tube methods, which have proved of little value in the determination of the viscosity at high temperatures. (2) a. Concentric cylinder method in which the inner cylinder is rotated at constant velocity. The range at high temperatures is about $10\text{-}10^7$ poise. This is a suitable method for measuring the viscosity of glasses and some blast-furnace slags at the lower temperatures. It is unsuitable for viscosity measurements of open-hearth slags. b. Concentric cylinder method in which the outer cylinder is rotated at constant velocity. It has been used in a range from 0.1 to 10^4 poise at high temperatures. It is suitable for measuring the viscosities of molten glasses, blast-furnace and open-hearth furnace slags. (3) Falling-sphere methods or methods depending on Stoke's law for the terminal velocity of a sphere falling or rising freely through a viscous medium. They have not been used with great

success until recently at high temperatures, due more to lack of refinements in the equipment than to defect in these methods. They are suitable for measuring the viscosities of molten glasses, but the range is too high for blast-furnace and open-hearth furnace slags. (4) Logarithmic decrement or torsion oscillation method which has a range from about 0.1 to 50 poise at high temperatures and is, therefore, suitable for open-hearth and blast-furnace slags. The theory, apparatus, procedure, errors involved, and advantages of each method have been described in great detail. Other relatively unimportant methods have also been briefly mentioned. 113 references.

The Viscosity of Slags and Glasses, Part II—Viscosity-Temperature Relationships and the Constitution of Molten Slags and Glasses.—J. R. Rait, *Trans. Brit. Ceram. Soc.* 40, (5) 205-229 (1941).

The literature on the relationships between viscosity and temperature and between viscosity and composition with particular reference to the constitution of liquids including molten slags and glasses has been reviewed. The paper, however, does not cover the literature on the viscosity of slags or glasses at low or at annealing temperatures.

Frenkel's fundamental equation for the viscosity-temperature relationship has been discussed in detail though the Eyring-Ewell treatment on the same subject has not been covered. (Summarized by R. H. Ewell, *J. Applied Physics*, 9, 252-269, (1938)). The fact that $\ln \eta - (1/T)$ plot does not result in a straight line for molten silicates has led investigators to suggest that a molten silicate is an associated liquid, the degree of association decreasing with increasing temperature. The relations between viscosity and vapor pressure and viscosity and electric resistivity have also been indicated.

Investigations on viscosity-composition relationships yielded controversial results. For the CaO-SiO_2 system, Hertz found a minimum on plotting viscosity against CaO-content, while McCaffery, Heidkamp and Endell and Rait and Hay obtained none. For the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, it was reported that discontinuities occur at compositions corresponding to changes of phase. Based on Preston's result on the $\text{Na}_2\text{O-SiO}_2$ system in which a series of minima were found for different temperatures on plotting viscosity against Na_2O -content, the author has stressed the existence of compounds in the molten glass. Apparently at the time of reviewing, Lillie's paper (*H. R. Lillie, J. Amer. Ceram. Soc.*, 22, 367-374, (1939)) which showed no minima in the same system was not at the author's attention. There is a

necessity for systematic measurements of slag systems of open-hearth furnace type.

No investigations were mentioned about the relationships for viscosity, temperature and composition combined.

73 references plus an additional note at the end of the paper.

The Viscosity of Slags and Glasses, Part III—The Relation Between the Viscosity of Slags and Their Attack on Refractory Materials.—J. R. Rait, and A. T. Green. *Trans. Brit. Ceram. Soc.*, **40**, (6), 231-269 (1941).

The literature on the relation between viscosity of glasses and slags and their attack on refractories has been reviewed. The solution of refractories by slags, or slagging, is the most common cause of refractory failure. The slagging is a complex reaction between a complex liquid and a heterogeneous solid, producing a material which melts at a lower temperature than the temperature of operation. Complete information about any reaction can be obtained only after thermodynamic and kinetic considerations. From the thermodynamic aspect, the chemical compositions of slags or glasses and of refractories are of chief importance. The solubility of the refractory in the attacking liquid expresses the maximum possible slagging. It is necessary to investigate the equilibrium condition for various slags or glasses and refractories, for if the equilibrium conditions produce no material melting at a temperature lower than that of the technical process, there can be no serious slag action. Unfortunately information concerning the equilibrium diagrams for slag and glass reactions with refractory materials has not yet been available. From the kinetic point of view, there are two rate processes that govern the slagging. The absolute reaction rate which depends on the chemical compositions of attacking liquid and refractory has not been discussed, but the rate at which fresh active slag makes contact with the refractory and at which the products of reaction are removed has been considered of major importance to slagging. Some of the factors controlling such rate are: (a) surface tension of the slag or glass; (b) wetting power of the slag; (c) viscosity of the slag; (d) melting point of the slag; (e) texture of the refractory; (f) thermal conductivity of the refractory; (g) emissivity of the refractory; (h) after-contraction and density of the refractory. Theories concerning viscosity and slagging have been reviewed in great detail. 131 references.

KUAN H. SUN.

Effect of Barium Oxide and Zinc Oxide on Properties of Soda-Dolomite-Lime-Silica Glass.—Contribution of the General

Research Laboratory, Owens-Illinois Glass Company. *J. Am. Ceram. Soc.* **25**, (3) 61-69 (1942).

The effect of the substitution of 1, 3 and 5% BaO and ZnO for (a) Na₂O, (b) Ca (Mg) O, (c) SiO₂ in the base glass 74% SiO₂, 12% CaO. MgO, 14% Na₂O on the viscosity as well as on other properties was investigated. Values between log viscosity = 3 and 7 cover the range which is of interest for the glass technologist.

(a) In the entire range of viscosities the substitution of either oxide for Na₂O increased the viscosity in a similar way.

(b) The effect of ZnO is almost entirely equal to that of dolomitic lime, but for a slight relative increase of viscosity in the high temperature—low viscosity area. Barium oxide, however, decreases the viscosity in the low temperature—high viscosity area, when substituted for CaO.MgO. Consequently, BaO increases the working range in comparison with ZnO and much more so in comparison with CaO.MgO.

(c) Substituting for SiO₂ either oxide decreases viscosity. The ZnO, however, has a smaller effect in the low temperature—high viscosity range; which again causes a relatively shorter working range of the ZnO glass than that of the corresponding BaO glass.

NORBERT KREIDL.

The Effect of Viscosity on the Melting Rate of Soda-Lime-Silica Glasses.—Eric Preston. *Jour. Soc. Glass Tech.* **25**, (110) 221-230 (1941)

It is surprising that a range of glasses of wide variation in composition originating from heterogeneous mixtures melts at a rate the temperature dependency of which is rather simply correlated to the viscosity-temperature curve. As a consequence of this correlation the "batch free time", that is the time required to obtain a glass melt free of any of the original constituents of the mixture, chiefly quartz grains, may be expressed by the linear equation:

$$\text{batch free time} = K \cdot \frac{\eta}{T - T_{\text{liq.}}} + C$$

The constant K depends on the size of the quartz grains, C on the experimental conditions, η is the viscosity at the temperature T; and $T_{\text{liq.}}$ is the liquidus temperature of the homogeneous glass resulting. The possibility of reaching such a simple approximation is based on the fact that, according to Turner and Preston, 90% of the melting time for glasses of this type is necessary for the dissolution of quartz grains, which is

undoubtedly governed by the rate of diffusion and, consequently by viscosity.

NORBERT KREIDL

LIQUIDS AND SOLUTIONS

The Viscosities of Liquids in Homologous Series—R. Linke, Z. Physik. Chem. A 187, 227 (1940).

The values of A and B in the Andrade-Sheppard equation, $\log \nu = A + \frac{B}{4.57T}$, (ν in stokes) were calculated for 7 n-paraffins,

11 n-alkylbenzenes, 6 n-alkylcyclopentanes, and 6 1-n-alkylcyclopentenes—1. The plot of the constants vs. the number of carbons gave a straight line for each homologous series. The deviations are small, except for the A values of the alkylbenzenes. The data given are: the A and B values which were calculated from viscosities available in the literature, and the straight line equations for calculating the A and B constants. The values of B increased, and the values of A decreased with the increase of the number of carbons, within the homologous series. For the alkylbenzenes, where the calculated A and B values had the greatest deviations from the observed values, the calculated viscosities differed at most, 10 per cent from the observed values. The straight line equations for $\log \nu$ vs. number of carbons, at constant temperature, were calculated from the straight line equations for A and B vs. number of carbons within a homologous series, for n-alkylbenzenes at 20° C. and for n-alkylcyclopentanes at 40° C. Until more data are available, these equations can be considered valid for only the lower members of the series covered.

J. M. GEIST

The Influence of Constitution on the Viscosity of Liquids—R. Linke, Z. Physik. Chem. A 188, 11 (1941).

The influence of constitution on the constants of the Andrade-Sheppard equation, $\log \eta = A + B/4.57T$ (η in poises) were discussed for known values of viscosities of hydrocarbons, mostly for the octanes. The data given are the A and B values and the temperature range over which the original measurements had been made. Tables are given showing the effect of the position of the substituted methyl groups on the values of A and B. The most symmetrical compounds have the highest A values, and A decreases with increasing dis-

tance between the substituted groups. The B values are lower the more symmetrical the compound, with the exception of tetramethyl butane, and increase with increasing distance between substituted groups.

J. M. GEIST

The Viscosity of Liquid Binary Mixtures—R. Linke, Z. Physik. Chemie, A 188, 17 (1941).

The viscosities, in poises, of the six binary mixtures between benzene, toluene, chlorobenzene, and cyclohexane, were determined at 10 mol per cent intervals, from 10 to 50 degrees Centigrade, and are given in tabular form. The constants of the Andrade-Sheppard equation,

$$\log \eta = A + B/4.57T \quad (\eta \text{ in poises})$$

are plotted against mole per cent, straight lines resulting for the aromatic mixtures, and various curves resulting for the mixtures of cyclohexane with the aromatics. By specifying that no change in molecular weight occurs in the solution, and that A and B in the Andrade-Sheppard equation are linear functions of concentration, it was shown that the following equation results:

$$\log \eta = n_1 \log \eta_1 + n_2 \log \eta_2$$

where η_1 and η_2 are the viscosities of the pure substances at temperature T, and n_1 and n_2 are their mole fractions.

J. M. GEIST

The Viscosity of Formamide-Dioxane Solution At 5, 25, and 40°—W. George Parks, I. Milton LeBaron and Everett W. Molloy. J. Am. Chem. Soc. 63, 3331-6 (1941).

The viscosities of mixtures of carefully purified formamide with 1, 4-dioxane and 1, 3-dioxane have been measured over the whole range of concentrations at 40 and 25°C, and from 28 to 100% formamide at 5°C. Non-linear curves were obtained showing maxima at approximately 91% formamide, which is taken as an indication of a compound of 1 mol of dioxane to 5 of formamide. Empirical equations for the densities of these solutions as functions of composition and temperature have been derived with a maximum error of 0.5%. Empirical equations were also derived for fragments of the viscosity-concentration curves.

Viscosity-composition curves have been drawn to compare

formamide-dioxane solutions with formamide and acetic acid, ethyl alcohol and water.

S. S. KISTLER

Variation of Viscosity of Cellulose Acetate Solutions With Concentration and Nature of Solvent—M. Takei and H. Erbing. *Kolloid Z.* 95, 207 (1941).

The variation of viscosity with concentration was determined for a sample of cellulose acetate dissolved in the following solvents: dichloroacetic acid, aniline, acetic anhydride, 2-methoxy ethyl acetate, ethyl lactate, and acetone. The same solvents had been used in a study of the dielectric properties of cellulose acetate solutions, in which it was established that there was neither appreciable association between chains nor variation in the degree of solvation within the concentration range studied.

It was found that the relationship between viscosity and concentration could be represented by the Bredee and deBooys modification of the Arrhenius equation:

$$\log \eta_{\text{rel}} = \underline{k} \cdot C_v = \underline{k}' C_v \cdot (1 + C_v + 0.1 \underline{k}' C_v)^{A-1}$$

The results could also be represented by the Philippoff equation:

$$\eta_{\text{rel}} = \left(1 + \frac{[\eta]}{8} C\right)^8$$

for the last three solvents named, but not for the first three. A modified Philippoff equation:

$$\eta_{\text{rel}} = \left(1 + \frac{[\eta]'}{8} C\right)^8, \quad \frac{1}{[\eta]'} = aC + \frac{1}{k}$$

represented all six sets of results within the experimental accuracy. The constants required in the above equations to fit the experimental data, listed in Table I, were compared with the function dipole moment squared divided by the product of dielectric constant and surface tension.

Table I

Solvent	Bredee and deBooys		Philippoff			$\frac{\mu^2}{\epsilon \cdot \sigma} \cdot 10^{-4}$
	k'	A	$[\eta]$	k	a	
Dichloroacetic acid	70.1	3.15		1.80	0.014	59.6
Aniline	79.4	3.25		1.32	0.012	85.8
Acetic anhydride	79.3	3.15		1.43	0.013	118.9
Ethyl lactate	73.9	2.73	1.24	1.28	0.0055	145.2
Methyl glycol acetate	72.4	2.83	1.26		0	154.8
Acetone	69.1	2.86	0.90		0	165.2

It is apparent from the table that there is a connection between this function and constants of the viscosity-concentration equations, high values of A and a being associated with low values of the function $\mu^2/\epsilon\sigma$

H. M. SPURLIN

POLYMERS

Molecular Size Distribution in Three Dimensional Polymers. I, II and III—P. J. Flory. *J. Am. Chem. Soc.* **63**, 3083, 3091 and 3996 (1941).

I. Gelation

Polymers formed from bifunctional units are invariably soluble and fusible. If units of higher functionality are present, gelation sets in suddenly at a sharply defined degree of reaction, after which the polymer is infusible and partially insoluble. Since gelation occurs only when there is the possibility of unlimited growth in these dimensions, the conclusion that it is the result of the formation of infinitely large molecules has been irresistible.

The general condition for the formation of infinitely large molecules is expressed by $\alpha > 1/(f-1)$ where f is the functionality of the polyfunctional "branch" units and α is the probability of chain branching as opposed to chain termination. The latter quantity can be computed from the relative concentration of branch units and the degree of reaction. When experimentally observed gel points in three dimensional condensation polymerizations are compared with theoretical critical points for the formation of infinite networks, calculated from the above criterion, the discrepancies are no larger than may be attributed to the formation of some intramolecular linkages, which are not accounted for in the theoretical treatment.

The analysis shows clearly that the number average molecular weight need not be very large when the statistical conditions for incipient formation of infinitely large three dimensional networks are fulfilled. Many smaller molecules are interspersed with the giant networks.

II. Trifunctional Branching Units

The distribution of molecular species of various complexities in three dimensional polymers in which the chain branching units are trifunctional has been investigated by statistical methods. The analysis shows that although increasing quantities of complex species are formed as the polymerization proceeds, simple single chains (containing no branch units) are

always in abundance. Even at the critical point for the formation of infinite networks, i. e., at the gel. point, one-fourth of the polymer by weight is composed of single chain species.

At the gel point the number average molecular weight \bar{M}_n is merely three-halves what it would have been if the trifunctional units had been replaced stoichiometrically with bifunctional units. On the other hand, the size distribution of species is broadened markedly by the presence of the branch units. This effect on the distribution is reflected by the rapid rise in the weight average molecular weight \bar{M}_w as the gel point is approached. In contrast with \bar{M}_n , \bar{M}_w reaches infinity at the critical point $\alpha = 1/2$, although no infinite networks are present until α exceeds $1/2$ (α equals the probability of a branch at the end of a given chain.) Since the viscosities of polymers depend on their weight average molecular weights, an explanation is provided for the observed increase in viscosity without limit as the gel point is approached.

The simultaneous presence of sol (soluble polymer) and gel (insoluble polymer) after gelation, is shown by the statistical treatment to be the direct consequence of random distribution of branch units in the polymer. It is in no way dependant upon different chemical properties of the ingredients from which the sol and gel fractions are formed.

For values of α greater than $1/2$, the weight fraction of sol is given by $(1 - \alpha)^2 / \alpha^2$. The weight fraction of gel can be calculated by difference.

Highly branched species are preferentially converted to gel as the reaction continues beyond the gel point. Consequently, the average complexity in the sol fraction decreases as the polymerization proceeds beyond gelation.

The situations dealt with in this paper and the one preceding find obvious analogies in certain gas phase chain reactions.

III. Tetrafunctional Branching Units

The distribution of species in three dimensional polymers composed of randomly cross-linked chains of uniform length can also be deduced by a somewhat different statistical method. The results parallel those of the preceding paper for trifunctionally branched polymers. Gelation occurs when the cross-linking index γ (equal to the number of structural units which are cross-linked per chain) is equal to unity, and the number average molecular weight is twice that of the chains.

The effect of non-uniformity in the length of the chains has been discussed. When the chains are randomly distributed in length, $\gamma = 1/2$ at the gel point.

P. J. FLORY

Viscosity and Molecular Weight of Chain-Like Molecular Substances—K. H. Meyer. *Kolloid Z.* 95, No. 1, 70-4 (1941).

A few years ago, Meyer and van der Wyk (*Kolloid Z.* 76, 278 (1936)) pointed out that Staudinger's rule was not valid for saturated hydrocarbons. The constant K_M showed a rather marked dependence upon M . However, these data did not extend further than to molecules containing 34 C-atoms. In the present paper, data on polypranes, polyprenes, vinyl derivatives, linear polyesters, and cellulose derivatives in various solvents are used to support the above criticism. The molecular weights range from 422 to 321,000. In all cases, as Professor Meyer points out, a marked decrease of K_M with increasing M is found. This is in qualitative agreement with Hibbert's and Flory's results respectively, (cf. *Rheology Leaflet No. 15*, 6, (1940); *Rheology Bulletin*, 12, No. 1, 12 (1941)).

One must agree with the author that conclusions about the internal flexibility of the dissolved molecule and its shape resulting therefrom can not be safely drawn on the basis of this rule. As discussed in the paper, the correct procedure would be not to extrapolate molecular weights in a homologous series, but rather to interpolate between a lower and higher polymer in the series.

It is felt, however, by the reviewer, that on the basis of the existing theories on the viscosity of solutions and our knowledge about the shape of flexible chains, it is possible to find, at least semiquantitatively, relations between specific viscosity and particle shape on the one hand, and shape and molecular weight on the other. It may be possible in this way to find also a quantitative measure for the degree of branching in the polymerization products.

At present, the Staudinger rule is a useful, because simple, prescription for a rapid estimation of a weight average molecular weight.

ROBERT SIMHA

Viscosity and Molecular Weight of Chain Polymers—K. H. Meyer. *Kolloid Z.* 95, 70-4 (1941).

The equation $K_M = \frac{\eta_{sp}}{C \cdot M}$ proposed by Staudinger to show

the constancy of the relationship between specific viscosity and molecular weight of a linear polymer has served as the basis for considerable work on the viscosity and structure of polymeric materials. The failure of K_M to remain constant for certain polymers, which from primary theoretical considerations should

have a linear structure, has been explained by other workers on the basis of branching of the structure of the polymer.

A critical review of the available data on viscosity and molecular weights of linear polymers does not, however, lead to agreement with the Staudinger equation or with conclusions drawn from it. A compilation of the existing data for a variety of chain polymers shows in every case a decrease in the K_M value for a homologous series as the molecular weight of the polymers increases. The systems which gave evidence of this variation are as follows:

1. Hydrocarbons

- Hydrogenated squalene or hydrogenated rubber in benzene or toluene
- Squalene or rubber type polymers in benzene or toluene
- Polystyrene in benzene

2. Substituted hydrocarbons

- Polyvinyl chloride in tetrahydro-furane
- Polyvinyl acetate in acetone
- Polyvinyl alcohol in water
- Polymethacrylate in acetone
- Polymethyl methacrylate in acetone

3. Linear polyesters

- Sebacic acid—hexandiol polyester

4. Cellulose and cellulose derivatives

- Cellulose in Schweitzers reagent
- Ethyl cellulose in chloroform
- Cellulose triacetate in m-cresol

Degradation reactions carried out on the polymers yield the same products for both the high and low molecular weight materials thus discrediting the theory that the low values of K_M obtained for the high molecular weight polymers are due to a difference in the fundamental structure of the polymer.

In view of the fact that the K_M value varies continuously with molecular weight in an homologous series, determination of the molecular weight of a polymer from its viscosity is possible only if one knows the viscosity and molecular weight of a lower and higher homolog of the same series. Extrapolation of the viscosity equation beyond known values is apt to lead to erroneous conclusions.

No absolute relationship between viscosity and molecular weight of polymeric materials is as yet known. Only a more

complete understanding of the kinetics of solvation will establishment of a true relationship be possible.

G. W. GERHARDT

Macromolecular Properties of Linear Polyesters. The Viscous Flow and Kinetic Interaction in Solution of ω -OH Undecanoic Self-Polyesters—W. O. Baker, C. S. Fuller and J. H. Heiss, Jr. *J. Am. Chem.* 63, 3316 (1942)

Polymers resulting from the self-esterification of ω -OH acids represent isochemical systems whose number average molecular weights can be unambiguously determined by end group titration. In addition they consist of molecules which are strictly linear and are of known molecular structure. They are therefore model macromolecular assemblies with which to test the Staudinger viscosity relations. This paper treats data obtained from fourteen members of the polymer-homologous series of self-polyesters of ω -OH-undecanoic acid with the following results:

(1) The relative viscosities of the several solutions at various molecular weights at various concentration were measured. The dependence of this concentration reduced relative solution viscosity upon concentration seemingly arises from articulation of the chain sections during flow.

(2) Viscosity determination on artificial mixtures demonstrate that the weight average molecular weight must be used in viscosity studies on inhomogeneous polymers. This had previously been shown by Kraemer & Lansing. (*J. Phys. Chem.* 39, 153 (1935).)

(3) The Staudinger viscosity constant K is strongly molecular weight dependant. If we use the alternative equation

$$\lim_{c \rightarrow 0} \left[\frac{\ln \eta_r}{c} \right] = K_w \cdot M_w + B, \quad K_w \text{ is satisfactorily inde-}$$

pendent of the molecular weight. If the chain length exceeds some minimum the constant B has similar values for several linear polymer series.

(4) Flow orientation was produced in concentrated solution by varying the shearing stress. This orientation, which gives rise to anomalous viscosities, depends on the average chain length.

HOWARD A. ROBINSON

RESINS

The Temperature Dependence of the Viscosity of Aniline Formaldehyde Resins in Cresol—Walter Scheele, Leonore Steinke and Irmgard Avisiers. *Kolloid Z.* 95, No. 1, 74-81 (1941).

It is shown that the T-dependence of η and η_{rel} can be expressed by a simple exponential formula $\frac{1}{\eta} = Ae^{-\frac{\epsilon}{KT}}$.

The parameters of this equation depends linearly upon the conc. (expressed in weight percent). The numerical results are:

$$\log \frac{1}{\eta} = 7.0 \cdot 10^{-2} c + 3.74 - (0.78 \cdot 10^{-2} c + 3.27 \cdot 10^3) \frac{1}{T} \cdot \log e.$$

$$\log \frac{1}{\eta_{rel}} = 7.0 \cdot 10^{-2} c - 0.78 \cdot 10^2 c \cdot \frac{1}{T} \cdot \log e.$$

These equations may prove helpful in the estimation of viscosities for such systems in a given concentration and temperature range.

ROBERT SIMHA

RUBBER

Dynamic Properties of Rubber.—S. D. Gehman, D. E. Woodford and R. B. Stambaugh. *Ind. Eng. Chem.* **33**, 1932-1038, (1941).

The work described in this paper was done by means of an electrically-driven vibrating machine, which could be operated at frequencies of several hundred cycles per second. The rubber samples were held in compression at a definite static deflection and were forced by means of the electrical system to vibrate about the position of equilibrium. The moving parts of the framework in which the samples were held was loaded with a series of weights, so that the condition of resonance could be reached at any particular frequency. The dynamic modulus and internal friction of the rubber stocks were measured from the natural frequency and mass of the system at resonance and from the amplitude at resonance, respectively.

The vibrating amplitude was studied as a function of frequency, and it was shown that, for gum stock, the agreement between the theoretical and experimentally determined resonance peaks was very good. In the case of stocks highly loaded with carbon black, the experimental peak was shown to be skewed. It was found that the internal friction was a rapid function of frequency. The dynamic modulus was, for loaded stocks, considerably greater than the static modulus, but did not appear to change with increases in frequency. The effect upon both the internal friction and the dynamic modulus produced by varying the loading of a number of different pigments was determined.

The work discussed in this paper appears to be done with

extreme care, and with recognition of the fact that loaded rubber stocks do not obey the simple differential equation of forced vibration with velocity damping and Hookean elasticity.

J. H. DILLON

THEORY

Fundamental Theory of the Dependence of Viscosity On Molecular Size and Molecular Shape

Presented at the P. I. B. Symposium, Feb. 20

by

Maurice L. Huggins

After a brief description of present-day concepts of the nature of liquids and liquid solutions, recent theoretical treatments, based on simplified models, of the viscosity of liquids are critically compared and contrasted. Possible extensions to more complicated models approximating the actual structures more closely are suggested.

Published equations for the viscosities of solutions and suspensions of spherical, elliptical, rodlike and kinked chain particles are compared, both as regards the assumptions and approximations made in their derivation and as regards their applicability to actual systems. The dependence of the viscosity on the size, shape, flexibility, electric charge, chemical nature, and concentration of dissolved or suspended particles and on the temperature and the nature of the solvent molecules will be carefully considered. Certain extensions and modifications of previous theoretical treatments are outlined and presented for discussion.

Viscosity, Molecular Size and Molecular Shape— Experimental Methods and Facts

Presented at the P. I. B. Symposium, Feb. 20,

by

Max A. Lauffer

Relationship of viscosity to the size of the molecules of related pure liquids and to the size or shape of the molecules of dissolved materials can be established on a purely empirical basis. The studies of Flory on molten linear polyesters have demonstrated exact relationships between the log of the viscosity and the square root of the weight average molecular weight of components of individual polymeric series. The early study of Staudinger and his collaborators and the more recent and more refined measurements of Signer, of Kraemer and his associates, of Meyer and van der Wijk, and of Fordyce and Hibbert have

shown conclusively that one can obtain approximately linear functions relating intrinsic viscosity to the molecular weight of many homologous series of chain-type particles dissolved in various solvents. Studies on proteins carried out by Polson, by Neurath and collaborators, by Oncley, and by the author have revealed that the viscosity of protein solutions can be definitely correlated with the shapes of the particles as determined by independent means. And finally, Eirich's viscosity measurements on suspensions of rod-shaped models of known dimensions have shown that the intrinsic viscosity increases with increasing axial ratios.

Available experimental data can also be used to test the applicability of various theoretically deduced relationships between viscosity and particle shape. The extensive studies of Eirich and his collaborators on the viscosity of suspensions of spherical models have shown conclusively the applicability of Einstein's equation defining the viscosity of a suspension of rigid spheres. It is not possible to over-emphasize the importance of this demonstration of the validity of the Hydrodynamic approach to the problem of the viscosity of suspensions. Huggins' extension of this treatment to randomly kinked chains of spheres has met with some success in accounting for the viscosity of some of the homologous rod-like substances. The hydrodynamic treatment as applied to rigid ellipsoids by Jeffery and as modified more recently by many individuals can be examined in light of the experiments on proteins and models. Three theoretical cases must be considered. 1. The case of complete Brownian motion—the category into which most of the protein solutions fall. The theoretical treatments of Simha and of Onsager lead to results in reasonable agreement with the experiments. 2. The case of no Brownian motion, exemplified by suspensions of models. The equations derived thus far for this case are not in satisfactory agreement with experimental observations. 3. The intermediate case—for example, solutions of tobacco mosaic virus. For these conditions, it can be predicted qualitatively from hydrodynamic theory that viscosity, at very low concentrations should be anomalous and that the temperature coefficient of relative viscosity should be **positive**. Robinson's experiments on tobacco mosaic virus confirm these predictions completely, thereby strengthening greatly the case for the hydrodynamic approach.

Note on Viscous and Plastic Flow.—N. A. DeBruyne. Proc. Phys. Soc. (London) 53, 251-7 (1941). The main types of viscous and plastic flow may be represented by a generalized

expression, relating velocity gradient and shearing stress, which is based on the assumed existence of a modulus of elasticity that is independent of temperature and of a relaxation time that varies exponentially with temperature. Values for the activation energy required to shift an atom or molecule from its normal position when derived from viscosity data agree well with those given by direct measurements of the times of relaxation. Constants are given for phenol-formaldehyde, o-cresol-formaldehyde, p-cresol-formaldehyde, m-cresol-formaldehyde, and m-5-xyleneol-formaldehyde resins. It is considered that the deformation of these resins under stress takes place by a change of molecular position from one stable state to another over an energy barrier equal to the activation energy. The maximum cohesive strength of a material may be deduced by equating the activation energy per unit volume to the work done on a unit volume in straining the material until the stress reaches its maximum value. Interaction between elastic strain energy and activation energy can account for some of the anomalous flow characteristics of amorphous materials, although such complicating factors as stress concentration due to inhomogeneity of materials may have to be taken into account.

E. C. HENRY

Virtual Masses and Moments of Inertia of Disk And Cylinders in Various Liquids.—Yei-Tak Yu. *J. Applied Phys.* 13, 66-9 (1942).

The effective mass or moment of inertia of an object in a fluid may be considerably greater than its value in a vacuum. For instance, the period of a torsion pendulum may be fifty per cent greater in water than in a vacuum, depending on its size and shape. Hence, many applied dynamical problems require the use of effective rather than actual values of mass or inertia, e. g., in the calculation of the power vs acceleration relations for a submarine or a dirigible. In this paper the author describes an experimental method, making use of a torsional pendulum, for determining the virtual moments of inertia and virtual masses of various objects moving in different liquids, and empirical results are reported for disks and cylinders in water, gasoline, and carbon tetrachloride, covering a density range of 0.734–1.574. Two identical test objects were mounted rigidly on the ends of a thin cross-arm, the midpoint of which was in turn rigidly fixed to a torsion wire. The determination of the free periods of oscillation of the pendulum in air (assumed to be the same as in vacuum) and in the liquid permitted the calculation of the virtual moment of inertia of the oscillating system, and hence of the virtual mass of the test object. It was

found that the virtual mass of a disk moving in a liquid normal to the plane of the disk is proportional to the density of the liquid and the cube of the radius of the disk. For motion in the plane of the disk, only the second power of the radius is involved. These relations are in qualitative agreement with theoretical calculation of Lamb, the experimental constants of proportionality being however larger than the theoretical values. Similar empirical results are presented for cylinders, but theoretical calculations are said not to be available for comparison purposes.

ELMER O. KRAEMER

Frictional Phenomena

by Andrew Gemant

(The Detroit Edison Company, Detroit, Michigan)

This series of articles, some of which have already been published and are abstracted below, is concerned with the present knowledge of viscous and related frictional processes, considered from a logical, unified standpoint. When complete, it will consist of three main parts covering, respectively, gases, liquids, and solids. Theories, experimental data, and technical applications in the field of mechanics, electricity and chemical technology are discussed.

Chapter I. Frictional Processes in General

J. Applied Phys. 12, 530 (1941)

In this introductory chapter a general and rather formal theory processes is presented that is valid, with certain restrictions, for all three states of matter. It is based on the existence of a viscosity constant that is independent of the rate of deformation. The theory, however, is useful also in cases for which this restriction does not hold since it is possible to define a corresponding, experimentally obtainable equivalent viscosity coefficient, whose variation with rate of deformation can then be investigated further. The fundamental differential equations that can be used for the computation of any particular case and the equations that show the amount of energy dissipated are further derived in this chapter and are illustrated by the flow of gas or a liquid between two parallel walls.

A. Gases

Chapter II. Theory and Experimental Facts on Gaseous Viscosity

J. Applied Phys. 12, 626 (1941)

On the basis of the kinetic theory an explanation is given of the viscous forces operative in a gas, and it is shown how the theory agrees with experimental facts on the dependence of gaseous viscosity on pressure, temperature, and chemical constitution. Next the theory of slip along walls is discussed including the influence of slip on the Poiseuille flow in tubes. The application of slip processes in certain vacuum pumps is discussed.

Chapter III. Absorption of Sound Waves and of Supersonics

J. Applied Phys. 12, 718 (1941)

The extent to which viscous processes can account for the absorption of freely traveling acoustical waves in gases is shown. Existing experimental data indicate a considerable divergence between theory and experimental data, particularly for polyatomic gases. An explanation of this divergence on the basis of intramolecular vibrations is presented, and illustrated by means of the variation of the absorption of supersonics in air with humidity and temperature.

Chapter IV. Sound Absorbing Materials

J. Applied Phys. 12, 725 (1941)

In this chapter a technical application of gaseous viscosity in the field of room acoustics is presented. After a brief introduction into the general principles of room acoustics, the absorbing property of sound-absorbing materials is explained on the basis of viscous processes in the pores of the material. Next the methods of measuring the flow resistance of absorbents are given. Experimental data on a number of materials are in fair agreement with the theory. It is even possible to derive by computation the characteristics required for the most efficient absorbent, important from the standpoint of their manufacture. Some practical problems in this connection, such as the reverberation of large rooms, the role of paint applied to absorbing panels, and the use of fiber glass as absorbent, close the chapter.

B. Liquids

Chapter V. Theory and Experimental Facts

J. Applied Phys. 12, 827 (1941)

This chapter presents theories of liquid viscosity particularly those of van der Waals, Andrade, Prandtl, and Eyring. Whereas the viscosity of gases is explainable by means of the collisions of molecules, that of liquids is dominated chiefly by molecular attraction forces. Hence the opposite signs of the temperature coefficient of gases and liquids. Experimental material is presented on the effect of chemical constitution, temperature, pressure and moisture-ratio on the value of the viscosity. Both temperature and pressure effects can be reproduced by exponential functions, as predicted by the theory. A brief exposure on turbulent flow in which inertia forces instead of viscous forces play a dominant role closes the chapter.

Chapter VI. The Measurement of the Viscosity of Liquids

J. Applied Phys. 13, 22 (1942)

A brief review of the principles and methods used for the measurement of the viscosity of liquids is given. First the capillary viscometers are dealt with, including the four chief corrections, i. e., end effect, kinetic energy, surface tension, and turbulence. Some of the most usual types are those of Ostwald, Ubbelohde, and Bingham-Murray. Next the Gemant-Southwell oscillation viscometer, based on oscillations of liquid columns in tubes, Couette viscometer, and the falling sphere method are discussed. A short discussion on the absorption of supersonics in liquids closes the chapter, and it is shown that there is a possibility of measuring viscosity on this basis, although the method has not yet been practically developed.

LETTERS TO THE EDITOR

Deformation of Elastic, Plastic and Viscous Substances.

Sir: In 1876 an American, J. Willard Gibbs, published "The Equilibrium of Heterogenous Substances." It received little recognition for a great many years, but was finally brought to the attention of the scientific world by a Hollander. In 1921 another American, P. G. Nutting, developed a general equation for the deformation of elastic, plastic and viscous substances¹, and presented the results of some experiments illustrating its application². It received little recognition for 20 years, but was finally brought to the attention of the scientific world during the past summer by an Englishman³.

Nutting considered Hooke's law of elastic deformation, and also Poiseuille's law of viscous flow. These laws may be stated:

$$(1) S = kF$$

$$(2) S = ktF, \text{ or } v = ds/dt = kF$$

By observing deformation in various bitumens, Nutting came to appreciate the dependence of the flow upon time; resistance continued to build up unless the material has been heated. The relation between the deformation and the time was a log.—log. one. On applying different forces, Nutting found that the relation between deformation and force was also of a similar nature.. These observations were then combined with (1) and (2):

$$(3) S = at^n \cdot F^m$$

All three of these equations are empirical. The constants are independent of S, t and F, but do vary with the temperature. If n is zero and m is unity, equation (1) is obtained, a special case of the Nutting equation. If both n and m are unity, another special case is Poiseuille's law. In Nutting's experiment, n varied between 0.2 and 0.9, while m varied from 0.9 to 3.5. When m was greater than 1 a plastic yielding was noted. When m was less than 1 he found a system with a quick-sand consistency. In all highly fluid liquids n approaches one. The melting point is the temperature where n approaches unity, while the freezing point is where n approaches zero.

Equation (3) can be expressed in a variety of ways. Scott-Blair³ is interested in food-stuffs and uses a logarithmic form. The log. of the deformation is called the "firmness" of the given substance. The effect of time on the flow or deformation is noted under constant stress. Other stresses are then applied and the firmness and other Nutting constants are calculated. The firmness of the foodstuffs is a very important factor in judging its properties and economic value. This is an extremely important conception, since it permits a direct tie-in, apparently for the first time, between the psychological "feel" of a system and its physical properties. The logarithmic relation between psychological perception and the physical intensities is common knowledge. Broome and Bilmes have used this equation, with interesting results, in the study of gunned asphalts⁴.

The importance of the "feel" of a substance is approached by workman skilled in the manipulation of a particular substance. The painter tells whether a pigment is properly proportioned by its resistance to stirring and the way it flows from his paddle. The plastics expert feels of a dozen samples of urea resin and predicts how they will behave in a molding process. The skillful farmer's wife knows when she has properly worked

her butter by the firmness. A brick mason said to the writer, "You may take all the mortars in the world to your laboratory, but the only way to tell the quality of the mortar is with this," shaking his trowel. He was quite correct for a proper degree of firmness is essential for effective brick laying, and adequate methods to evaluate it remain to be developed.

In order to obtain significant results to use in the Nutting equation, great care must be used in choosing the conditions for the experiment. Only one factor must be allowed to vary at one time. The temperature must be adequately controlled, of course, and the stress should remain constant during the application of the load. Scott-Blair has developed a special apparatus for this purpose.

In the general testing of materials, the rate of loading is usually specified, since its effect on the "ultimate" strength is generally appreciated. When plastic substances are loaded at different rates a family of stress-strain curves is usually obtained, each having a particular inflection point. It has often been the custom to call such an inflection point the "yield point," but since it varies with the rate of loading, it might be more logical to speak of it as a "yield front" (like the current line of fighting in Russia). It is to be deplored that the conception of yield point has become so firmly fixed in our thinking.

It is strongly urged that all interested in Rheological systems should study carefully the contributions of Nutting Scott-Blair and Broome and Bilme. The present test methods should be carefully scrutinized to insure adequate control of conditions. The exponents in Nutting's equation should be calculated, as well as Scott-Blair's firmness. Certain limitations will doubtless be found; for instance, Scott-Blair has observed that crumbly cheeses do not follow this law, nor do the elastomers, such as asphalt-rubber mixes. Other limitations will doubtless be discovered, but this method of attack upon Rheological problems offers the most promise of leading to their understanding.

It is respectfully suggested that the Nutting equation offers an extremely promising working hypothesis for the attack of a large number of Rheological problems and that a symposium might be advantageously organized for the discussion thereof.

F. O. ANDEREGG
51 Charles Street
Newark, Ohio

¹ P. G. Nutting, "New Law of Deformation," *J. Franklin Inst.* 191, 629 (1921).

- ² P. G. Nutting, "A Study of Elastic and Viscous Deformation," **Proc. Am. Soc. Testing Mats.** 21, 1162 (1921)
- ³ G. W. Scott-Blair and F. M. V. Coppen, "Measurement of the Firmness of Soft Materials," **J. Soc. Chem. Ind.** 60, 190 (1941).
- ⁴ D. C. Broome and L. Bilmes, "Rheological Properties in Gunned Asphalts," **Ibid**, 60, 184 (1941).

APPLICATION

R. B. DOW, Secretary-Treasurer
Ballistics Research Laboratory
Aberdeen Proving Ground, Maryland.

I hereby apply for membership in the Society of Rheology commencing January 1 as follows:

Sustaining membership (including subscription to Rheology Bulletin, Journal of Applied Physics, and Review of Scientific Instruments.) \$25.00 or more.

Subscribing membership, (including subscription to Rheology Bulletin and Journal of Applied Physics.) \$7.00 (foreign, \$7.70)

Membership, (including subscription to Rheology Bulletin.) \$2.00

Please also enter my subscription for the following additional periodicals published by the American Institute of Physics, at the rates available to members of the five founder societies:

Review of Modern Physics\$3.00 (foreign, \$3.40)

Review of Scientific Instruments.....\$3.00 (foreign, \$3.50)

Journal of Chemical Physics.....\$10.00 (foreign, \$11.00)

I enclose \$.....to cover the above.

Name.....
(Please print)

.....
Title

.....
Corporation or School

.....
No.

.....
Street

.....
City

.....
State

