

ΠΑΝΤΑ



ΣΕΙ

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RHEOLOGY BULLETIN

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SOME REMARKS ON THE MOLECULAR MECHANISM OF VISCOUS FLOW

TURNER ALFREY

INTRODUCTION

ONE OF THE most important contributions of recent years to the theory of viscous flow has been the approach by Eyring and his coworkers.¹ This approach (based upon the concept of liquid structure as being essentially a "mixture of molecules and holes") has become widely accepted and undoubtedly reveals some of the most significant aspects of the flow process.

At a recent seminar at the Polytechnic Institute of Brooklyn, Professor Eyring presented a comprehensive review of this theoretical approach. In the course of the subsequent discussion certain minor geometrical objections were raised to the specific model employed in the theory. While these points in no way invalidate the general results of the theory, it was felt that it would be worth while to clarify the geometrical aspects of the problem in this communication.

I. SUMMARY OF THE HOLE THEORY OF LIQUID FLOW

Much evidence points to the fact that in a liquid the nearest neighbors of a given molecule are (mainly) arranged about it in a fashion very similar to that of the crystalline state—but that this local order does not extend very far through the liquid. This fact, together with the increase in volume of a crystal on melting, leads very definitely to the idea that the liquid structure contains many gaps or "holes." In the theory under consideration, it is assumed that all these holes are the same size, or, more precisely, that they can be adequately characterized by a single "average size." This is a very reasonable approximation which introduces no ambiguity.

A molecule situated next to a hole is considered to have two possible equilibrium positions, separated by a potential energy barrier (see Fig. 1). Passage over this barrier corresponds to the process of jumping into the adjacent

¹ H. Eyring, *J. Chem. Phys.*, 4, 283 (1936); R. H. Ewell and H. Eyring, *J. Chem. Phys.*, 5, 726 (1937); S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes*, McGraw-Hill, New York, 1941.

hole. This is an elementary process of diffusion; after a molecular jump, the hole is in a new location, and some other molecule can jump into it, etc.

It is implicitly assumed that this elementary process is a *local* structural change in a rigid surrounding matrix. There is no simultaneous rearrangement of the sample as a whole—any macroscopic changes are the result of many cumulative local jumps.

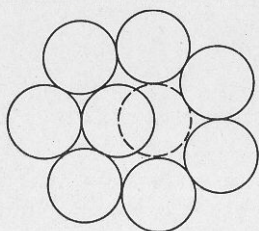


Fig. 1.—Liquid molecule adjacent to hole.

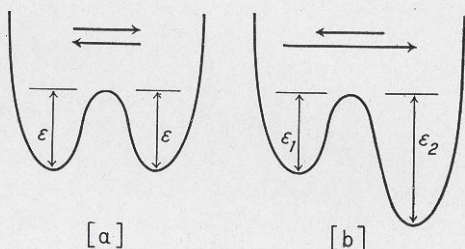


Fig. 2.—Potential energy curves.

In the absence of a stress, jumps in all directions are equally frequent, so that, while there is diffusion, there is no flow. It is assumed, however, that a shearing stress will bias the potential energy curve (as shown in Fig. 2a) into the form shown in Figure 2b. Such a bias makes “forward” jumps more frequent than “backward” jumps, resulting in a net forward velocity of the layer under consideration. The stress-biased jumping of molecules into neighboring holes is thus advanced as the molecular origin of viscous flow. The elementary processes of flow and diffusion are considered as identical.

II. STATEMENT OF CERTAIN GEOMETRICAL CRITICISMS OF THE ABOVE PICTURE

A. A stress field must be recognized as distinct from a force field. A stress must be represented mathematically by a tensor of the second order—a dyadic; a force can be represented by a tensor of the first order—a vector. The mechanical effects of a stress field are geometrically more complicated than those of a force field.

Specifically, the presence of a stress at a given point does not cause a net force to act upon a molecule at that point. If a molecule which is adjacent to a hole, as in Figure 1, has a potential energy curve similar to that in Figure 2a, the symmetry of this curve will not be affected by the presence of a stress. *The stress will not change the relative frequency of jumps in opposite directions, and hence will not lead, through this mechanism, to any net motion of the layer containing the hole.*

The presence of a stress does indeed bias the potential energy curve for a molecule situated next to a hole, and hence must bias the process of diffusion which takes place by the mechanism of molecules jumping into adjacent holes. The nature of this bias will be discussed in Part III; it does not lead to flow.

B. Strain, like stress, has the character of a dyadic, whereas displacement and velocity have the character of vectors. Even if (contrary to the statements in A) it is assumed that jumps in the forward direction are more frequent than jumps in the backward direction, the preponderance of forward jumps is not equivalent to viscous flow. A forward jump results in a *displacement* of the containing layer relative to the surrounding rigid matrix, *i.e.*, relative to *both* the adjacent layers. No *strain* has been established, however, and hence no *flow* results from a repetition of the process. In viscous flow, a layer moves in the positive direction relative to one adjacent layer and in the *negative direction relative to the other adjacent layer*. That is to say, flow implies a *velocity gradient*. An inequality in the frequency of forward and reverse jumps, in the model described in Part I, would result in a net *translation* of the sample, but not in flow.

C. We have stated that a stress will not affect the frequency of forward and reverse jumps in a model such as is shown in Figure 1, and that even if such a response were to occur it would not correspond to viscous flow. What, then, is the mechanism of viscous flow?

The unit molecular process involved in viscous flow must have a *rotational* character. If we wish to retain the concept that this elementary process consists of a local rearrangement of molecules, taking place in a rigid surrounding matrix, then we are forced to the conclusion that the process involves the rotational motion of a molecular *cluster* (relative to the surrounding matrix). In the absence of a stress, rotational jumps of temporary pairs, triplets, etc., of molecules will take place alongside the translational jumps of individual molecules, and will contribute to the diffusion. In the presence of a stress, these rotational jumps will be biased in such a fashion as to relieve the stress, and to produce flow.

D. These geometrical remarks do not necessarily constitute a criticism of the theory of flow described in Part I. The replacement of second-order tensors (stress and strain) by vectors (force and displacement) is a legitimate schematic condensation of the actual complicated situation, just as a one-dimensional potential energy curve is a legitimate condensation of a multidimensional potential energy surface and is often very useful in the discussion of a rate process. The essential features of the theory of flow remain unchallenged. Presumably the only effect of these remarks would be on the molecular interpretation of the constant which, in the theory (Part I) is written as $\lambda_1\lambda_2\lambda_3$.

It should be remarked that, in an early paper,² Ewell and Eyring con-

² Cf. p. 729 of reference 1.

sidered the rotational jumping of temporary clusters as a possible mechanism of viscous flow. The tendency has been, however, to conclude, on the basis of quasithermodynamic data, that the dominant mechanism is the jumping of single molecules.

III. DETAILED GEOMETRY OF FORCE AND STRESS FIELDS

This section is concerned with the specific geometrical nature of the bias which force fields and stress fields impart to the effective molecular potential energy curves and to the elementary processes of diffusion.

1. Isolated Holes—Translational Jumps of Single Molecules

Consider first the case of a single isolated hole. A molecule adjacent to this hole has two possible equilibrium positions, which are separated by a region of high potential energy. Let the displacement of the molecule along the line connecting the two equilibrium positions be taken as a deformation coordinate, x . The potential energy as a function of x can be represented by a curve of the form indicated in Figure 3a.

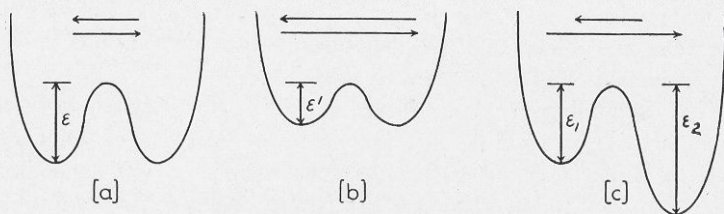


Fig. 3.—Potential energy curves.

Effect of an External Force

If the molecule under consideration is now subjected to an external force field, the potential energy curve of Figure 3a will be deformed in the manner shown in Figure 3c. One equilibrium position becomes more stable than the other. The activation energy for a “forward” jump (ϵ_1) becomes different from that of a “backward” jump (ϵ_2). For example, if the molecule under consideration has a greater weight (but similar volume) than the molecules which constitute the surrounding matrix, then a strong gravitational field will cause such a deformation of the potential energy curve. If the direction of the field makes the angle θ with the coordinate x , then the magnitude of the deformation ($\epsilon_2 - \epsilon_1$) would presumably be roughly proportional to $g \cos \theta$.

The result of this force, pulling the molecule in the positive direction, is to make forward jumps more frequent than backward jumps. Over a long period of time the heavy molecule will exhibit a net translational motion relative to the matrix.

This process necessarily involves the presence of two kinds of molecules which are acted upon with different intensity by the force field. If all the molecules are pulled with the same force, then as soon as the quasirigid matrix achieves elastic equilibrium the field acting upon any small region is not a force, but a stress, which will be discussed in the next paragraph.

Effect of a Stress

The effect of a *stress* upon the potential energy curve of a molecule with two equilibrium positions is quite different from the effect of a *force*. A stress causes the potential energy curve (Fig. 3a) to be deformed in the fashion indicated in Figure 3b. The activation energy for the jump is changed from the unstressed value, but *the curve remains symmetrical*. The activation energies for forward and backward jumps are still equal to each other. The magnitude of the change ($\epsilon' - \epsilon$) is a function of the values of the components of the stress tensor. The nature of this function will depend in a detailed way upon the structure of the material.

As a result, the rate of molecular jumping will be different in different directions. Hence, the diffusion constant (in so far as diffusion follows this mechanism) will be different for different directions in the liquid. The rate of diffusion in any two *opposite* directions, however, will be equal.

2. Multiple Holes—Rotational Jumps of Molecular Clusters

Consider now the case of a pair of adjacent molecules which can simultaneously jump to new equilibrium positions, causing a *rotation* of the pair within the rigid surrounding matrix. This is indicated in Figure 4. (Larger clusters will not be explicitly considered.) The angle θ between the line of centers of the two molecules and some external coordinate axis can be considered as a deformation coordinate for the molecular pair. The potential energy as a function of θ will be of the form shown in Figure 3a. In the absence of a stress, "forward" and "backward" rotational jumps will be equally frequent. After such a jump, the pair need not retain its identity; the molecules can "change partners" and make new rotational jumps as members of new clusters, or can simply diffuse away from each other by translational jumps into single holes.

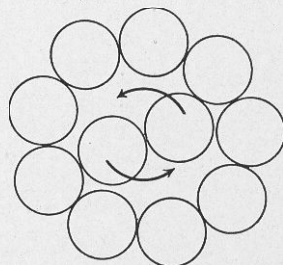


Fig. 4.—Pair of molecules with opportunity for rotational jump.

In the presence of a shearing stress, the potential energy curve shown in Figure 3a will be deformed in the fashion indicated in Figure 3c. This will result in a preponderance of rotational jumps in the "forward" sense—*i.e.*, the sense which most nearly aligns the pair in the direction of the largest principle tensile stress.

Multiple repetition of this mechanism results not only in a net velocity, but in a *velocity gradient* at the point in question. It is, therefore, consistent with the hydrodynamic requirements for viscous flow.

ABSTRACTORS IN THIS ISSUE

The following collaborators have cooperated in making this February 1945 *Rheology Bulletin* a success.

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BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY (B.I.P.C.)

RHEOLOGY PROGRESS ABSTRACTS

APPARATUS AND METHODS

THE BEHAVIOR OF PLASTIC MATERIALS UNDER REPEATED STRESS.

B. J. LAZAN and A. YORGIADIS, *Modern Plastics*, **21**, 119-28, 164 (1944).

An adequate engineering analysis of a material is no longer possible when only the usual static properties are known; complete information on the behavior of materials under vibrations is now an acknowledged necessity. The rapid development of structural plastics has not been accompanied by a correspondent development in dynamic testing techniques. Usually it has been necessary to employ machines developed primarily for testing metals. In the present paper, special emphasis is placed on many important differences between metals and plastics and the significance of these differences as related to dynamic testing is discussed. The following basic dynamic tests are covered: damping capacities, dynamic moduli of elasticity, and fatigue strength. The procedures employed and their limitations are outlined: results of available data are given in several curves and one table. 37 references. B.I.P.C.

A BIBLIOGRAPHY OF ELECTRON MICROSCOPY.

CLAIRE MARTON and S. SASS, *J. Applied Phys.*, **15**, 575-9 (1944); cf. B.I.P.C., **14**: 86.

This is a supplement to the previous bibliography in an attempt to bring it up to date and to include foreign references previously not available.

B.I.P.C.

AUTOMATIC STIRRER FOR VISCOUS LIQUIDS.

Bell Lab. Record, **22**, 521 (1944).

Stirring action in a viscous liquid is accomplished by a steel plunger inside a glass tube. The glass tube is oscillated in an electromagnetic field which moves the steel plunger in the viscous liquid.

BITUMINOUS MATERIALS

RHEOLOGICAL PROPERTIES OF ASPHALT.

R. N. TRAXLER, H. E. SCHWEYER, and J. W. ROMBERG, *Ind. Eng. Chem.*, **36**, 823-829 (1944).

The flow characteristics of twenty-seven asphalts from different sources and processed by various methods are evaluated in rotary viscometers of a type suitable for the measurement of high consistencies at a constant rate of shear. Consistencies of each asphalt at fixed temperatures were determined at two or more mean rates of shear. If an asphalt is a complex liquid, the measured consistency decreases as the rate of shear is increased. The magnitude or degree of complex flow may be evaluated by c in the equation, $M = F/S^c$; c is unity for asphalts that are simple (Newtonian) liquids but varies from unity for those that are complex liquids. This equation is valid over a considerable range in rate of shear and is not limited to one type or size of viscometer. Data are given which show that certain asphalts are simple liquids

at service (atmospheric) temperatures, while others have the characteristics of complex liquids. Evidence is given that the type of flow (and if complex, the degree) depends on the source of the asphalt, the method and degree of processing, the age of the sample, and the temperature at which the evaluation is made. It is shown that some asphalts retain their complex flow characteristics at temperatures as high as their ring and ball softening point. The relations between the fundamental rheological characteristics of asphalts and the empirical tests commonly used by bituminous technologists are illustrated.

AUTHOR'S ABSTRACT.

DISPERSIONS

THE MEASUREMENT OF FOAM STABILITY.

A. P. BRADY and SYDNEY ROSS, *J. Am. Chem. Soc.*, **66**, 1348-56 (1944).

The present paper is an attempt to show how far the stability of foams may be determined, independent of the particular method of measurement. The theory of foam measurement is analyzed and the factors are estimated which operate to make one foam differ from another; the resulting mathematical equations are tested by the experimental data presented. A foam meter for the measurement of foam stabilities at different temperatures is described, employing bubbling as the method of producing the foam. Foam stabilities of several types are measured and reported. The unit L_g (the average lifetime in minutes of gas in the foam) can be converted into a function that expresses the static foam stability of a liquid. For foams of the same character, this function is independent of temperature, viscosity, amount of liquid sample taken, method of producing foam, and dimensions of the apparatus. The relation between dynamic and static methods of foam measurement is pointed out.

B.I.P.C.

CAN THE CERAMIST USE EMULSIONS?

L. GRUPELLI, *Bull. Am. Ceram. Soc.*, **23**, 288-90 (1944).

The theory of emulsions is briefly presented. Different types, such as oils, resins, and waxes, and their properties are discussed. The author makes particular reference to possible application in structural clay product manufacture, particularly as an aid to the extrusion process.

J. A. PASK

PROPERTIES OF ENAMEL SLIPS. I. General Properties of Clays and Enamel Slips.

B. W. KING, JR., H. D. CARTER, and H. C. DRAKER, *J. Am. Ceram. Soc.*, **27**, 253-260 (1944).

Five clays used to suspend porcelain enamels were studied to determine crystal form, particle size, hydrogen-ion concentration, carbon content, and weight loss on heating. These clays were milled in different proportions with several types of porcelain enamel frits. The properties of the resultant slips were studied. The pickup weight, that is, the amount of enamel retained on a ground-coated plaque which had been dipped in the slip and allowed to drain, was used as a basis of comparison.

J. A. PASK

STUDY OF FACTORS INVOLVED IN GLAZE-SLIP CONTROL.

I. Glaze-slip Specifications. II. Correlation of Glaze Thickness with Air Permeability. III. Additional Glazes and Improved Technique.

C. G. HARMON with C. F. SCHAEFER, M. K. BLANCHARD, and H. C. JOHNSON, *J. Am. Ceram. Soc.*, **27**, No. 7, 202-20 (1944).

I. Experiments were conducted to find a simple, adequate means of specifying glaze consistency. Tests showed that the amount of slip clinging to a glass plate after it is withdrawn from a reservoir of slip (known as its coherence value) was directly influenced by such factors as amount of water, clay content, and age. These factors are commonly thought of as governing the working quality of the slip. Surface tension has little apparent relation to the working qualities of the slip. Examination of the fired glazes revealed that a distinct coherence value of less than 0.04 g. per sq. cm. separated good glazes from poor types.

II. An adequate correlation was obtained, independent of the type of body, between thickness of glaze deposition, glaze consistency (coherence value), and water receptivity. No general correlation was found between thickness of deposition of glazes and the air permeabilities of the bodies.

III. Improvements in technique and apparatus are described. The correlation between glaze consistency, body receptivity, and thickness of deposition is represented by a simple first-order equation having two constants:

$$P = K \left(\frac{R}{100} \right) (C - 0.001)$$

wherein P = pickup, K = deposition constant, R = receptivity, and C = coherence value.

IV. Practical uses for coherence-value and receptivity measurements are suggested as: (1) a check on incoming raw materials, (2) a basis for selection of certain raw materials, (3) a control test for slip consistency, (4) a control test at various steps in the manufacturing process, and (5) a basis for blending clays and other raw materials. These methods are also said to hold promise of general application in fields other than glaze control.

J. A. PASK

RATE OF SEDIMENTATION; SUSPENSIONS OF UNIFORM-SIZE ANGULAR PARTICLES.

H. H. STEINOUR, *Ind. Eng. Chem.*, **36**, 840-7 (1944); *cf.* B.I.P.C., **14**, 422.

Rates of sedimentation are reported for suspensions of closely sized emery particles, both flocculated and nonflocculated. Except for the value of an experimental constant, one rate equation applies to both states, provided the flocculated suspensions are highly concentrated. Comparison with previous tests on uniform spheres indicates that a portion of the liquid suspension medium is carried down with the angular emery particles during their fall, whether the suspensions are flocculated or not. The question as to whether this liquid is bound to the particles or is simply stagnant is studied, and evidence is shown to support the latter view. 13 references.

B.I.P.C.

THE FORMATION OF BUBBLES.

R. B. DEAN, *J. Applied Phys.*, **15**, 446-51 (1944).

Extreme values for the negative pressures and the degrees of superheat which water will withstand without forming bubbles are contrasted with the ease of forming bubbles by vibration or by turbulent flow of liquids. The subject of bubble nuclei is briefly reviewed, and it is pointed out that such nuclei usually function by virtue of sorbed or trapped air which can be removed, rendering the nuclei ineffective. A technique for avoiding extraneous bubble nuclei is presented with some experiments on the formation of bubbles by mechanical action. It is pointed out that free vortices in liquids produce sufficient tension to rupture the liquid, and it is suggested that mechanical disturbance produces bubbles only in such vortices and not by general pressure lowering in sound waves. 30 references. B.I.C.P.

FOAM FORMATION IN ORGANIC LIQUIDS.

E. GRAY KING, *J. Phys. Chem.*, **48**, 141-54 (1944).

The investigations reported in this paper were conducted to determine whether foams comparable in volume and stability to aqueous foams could be produced in organic liquids. It was found possible to produce such foams, liquids with surface tensions higher than those of the common volatile solvents appearing to be more susceptible to foam propagation. There are some indications that certain solvents have a greater tendency to support foam formation than other solvents of comparable surface tension. It is possible, on the other hand, that diligent search will reveal for every solvent a chemical structure which is an efficient foaming agent. Foaming is usually accompanied by a decrease in surface tension, but the converse is not always true. Physical properties, such as vapor pressure and viscosity, do not seem to be factors in foam initiation, but they influence the stability of the foams once they are formed. Several types of colloidal electrolytes have been proved to be surface active in organic liquids. The extent of their surface activity and also their propensity for foam formation may reside in a structural balance between the solute and the solvent. 18 references. B.I.P.C.

INHIBITION OF FOAMING IN SOLVENTS CONTAINING KNOWN FOAMERS.

SYDNEY ROSS and J. W. MCBAIN, *Ind. Eng. Chem.*, **36**, 570-3 (1944).

The foaming of liquids is a frequent cause of trouble in industrial and laboratory processes. Practically every industry has the twofold problem of suppressing undesired foams and of stabilizing foam where it is wanted. Methods of prevention or reduction of foam may be divided into mechanical and chemical. In the present article, a series of experiments is discussed which were aimed at determining the effect of incorporating certain agents in different well-defined systems capable of forming foam. The object of the investigation was to uncover some operative factors in the inhibition of foaming by means of antifoaming additives. The results indicate that the chemical inhibition of foaming may be accomplished by more than a single mechanism. Tabulated data of the effect of additives are included. 10 references. B.I.P.C.

CHEMICAL RUSSIAN, SELF-TAUGHT. I. Suggestions for Study Methods.

JAMES W. PERRY, *J. Chem. Education*, **21**, 393-8 (1944).

Continual increase in the volume of chemical research published in Russian confronts English-speaking chemists with the problem of acquiring a reading knowledge of chemical Russian without undue expenditure of time and effort. The program of study proposed by the author reduces the time spent on the grammar to a minimum, while emphasizing the advantages of an early beginning in reading chemical Russian. An elementary inorganic chemistry text is shown to afford an excellent means for acquiring familiarity with the vocabulary, idioms, and sentence constructions which characterize chemical Russian; this should be followed by attempting to read current chemical Russian journals. A year's spare time suffices for a practicing chemist to acquire a useful reading knowledge.

B. I. P. C.

GLASS

OBSERVATIONS INDICATING ABSENCE OF PLASTIC FLOW IN GLASS COATING ON STEEL.

W. G. MARTIN and F. W. LAUCK, *J. Am. Ceram. Soc.*, **27**, 352-4 (1944).

Steel rings were glass-coated to a thickness of 0.010 inch; some were split at one point immediately and others one or two years later. Identical movement of all rings caused by compressive forces in the glass indicated that no plastic flow takes place in the glass. The compressive forces were calculated and found to be of the general order of 10,000 p.s.i.

J. A. PASK

EFFECT OF SUBSTITUTING MgO FOR CaO ON PROPERTIES OF TYPICAL SODA-LIME GLASSES.

OWENS-ILLINOIS GLASS COMPANY GENERAL RESEARCH LAB., *J. Am. Ceram. Soc.*, **27**, 221-5 (1944).

In base glasses containing: (a) Na₂O 16, CaO 10, and SiO₂ 74%; and (b) Na₂O 14, CaO 12, and SiO₂ 74%, MgO was substituted in steps of 2% for CaO. Replacement of CaO by MgO results in an increase of viscosity at high temperatures for both series of glasses throughout the respective composition range. This substitution produces little or no effect on the low-temperature viscosity for compositions up to the dolomitic-lime ratio, but a definite increase in viscosity occurs in compositions having a higher MgO content. This is true for both the 10% and 12% lime glasses.

PAINTS

EFFECT OF COMMON ORGANIC ACIDS ON THE VISCOSITY OF ENAMELS CONTAINING ZINC OXIDE—D.C.I.C. CLUB.

MCSWEENEY, *Am. Paint J.*, **29**, No. 5B, 6-7 (1944).

The effects of sixteen organic acids on the viscosity of a zinc oxide alkylid enamel were studied. Simple unsaturated acids increased the viscosity

only slightly. Saturated acids caused greater increases, in some cases resulting in gelation. Naphthenic and abietic acids lowered the viscosity slightly. Chinawood oil acids and two of three dimeric acids caused rapid increases in viscosity to solid gels.

C. K. BUMP

PETROLEUM PRODUCTS

VISCOSITY DETERMINATION OF LUBRICATING OILS FOR AUTOMOTIVE SERVICE AT LOW TEMPERATURES.

R. SEUFERT, *Oel u. Kohle*, **40**, 23 (1944).

The following methods for the determination of flow behavior at low temperatures are compared: U-tube (German Railroad cold test); pour point (DIN); flow beginning (modified Vogel-Ossag viscometer); viscosity determination in Schwaiger (conc. cylinder) apparatus; and Höppler (rolling ball) viscometer. The well-known influence of thermal and mechanical pretreatment was again noted, requiring close adherence to standardized procedure. Above the cloud point, all viscosity measurements gave identical results independent of sample history. Below the cloud point, each viscometer gave different results and considerable variation in sensitivity to sample history. [Both these findings are of course due to the fact that each instrument subjects the oil to a different shear stress, causing widely varying degree of breakdown of paraffin wax structure. *Rev.*] The test instrument must thus be chosen to fit the expected service conditions as to applied shear stress in order to obtain results of practical significance.

A. BONDI

THE (VISCOSITY) POLE HEIGHT, AN ADDITIVE QUANTITY.

H. BROCKMANN, *Oel u. Kohle*, **40**, 23 (1944).

As had been shown by the reviewer several years ago [*Petroleum Z.*, **34**, No. 6, 1 (1938)], the author finds that the viscosity pole height (VPH) of lubricating oil mixtures can be predicted from the VPH of the components by the arithmetic mixing rule. This additivity holds for the common grades of lubricating oil only. It is not applicable to mixtures of widely differing petroleum fractions or nonhydrocarbon materials, and has no theoretical justification.

A. BONDI

FRICTION FACTORS FOR PIPE FLOW.

LEWIS F. MOODY, *Trans. A.S.M.E.*, **66**, 671 (1944).

A graph is presented for the evaluation of the Darcy-Weisbach friction factor f as a function of the Reynolds number (Re) and the relative roughness ϵ/D of pipes. The relative roughness function given by Colebrook,

$$1/\sqrt{f} = -2 \log (\epsilon/3.7D + 2.51/Re\sqrt{f})$$

where ϵ = absolute roughness [1], was used to construct this chart. The relation between relative roughness and pipe material, as well as a number of other graphs to facilitate hydraulic calculations, is also presented. An extensive discussion follows this paper. Participants: R. L. Daugherty, C. W. Hubbard, A. T. Ippen, W. S. Pardoe, R. J. S. Pigott, H. Rouse, and P. H. Schweit-

zer. Salient features of discussion: A. T. Ippen suggests writing Colebrook's equation as:

$$1/\sqrt{f} = 1.74 - 2 \log (\epsilon/r)(1 + 0.282 \delta/\epsilon)$$

where r = radius of pipe and δ = thickness of laminar boundary layer. Since δ is a function of the viscosity of the fluid, the relation between pipe friction phenomena and viscosity is thus brought out. The importance of viscosity for the magnitude of boundary shear and, consequently, the introduction of temperature as a third independent variable was discussed by W. S. Pardoe. R. J. S. Pigott finds that f becomes constant, *i.e.*, independent of Re at a value for $Re = 3500/(\epsilon/D)$. H. Rouse presents a graph of the Karmán-Prandtl relation by plotting $1/\sqrt{f}$ vs. $Re\sqrt{f}$ and D/ϵ in preference to Moody's mode of presentation. P. H. Schweitzer warns of the use of any of the presented relationships for any but "long" pipes, because the length of "short" pipes is insufficient to change the nature of flow which existed in front of the entrance zone to the one corresponding to the dimensions of the "short" pipe. The permissibility of application of the derived relations to the calculation of open-channel friction and the eventual necessity for introduction of the Froude number as a new criterion (to account for the surface effects) into this problem were also discussed.

A. BONDI

PRESSURE DROPS IN GRANULAR BEDS.

A. O. OMAN and K. M. WATSON, *Natl. Petroleum News*, 36, R-795 (1944).

The pressure drop in beds of uniformly sized granular particles is determined experimentally for a variety of typical particle shapes and various methods of bed preparation. It was found that the denseness and randomness of packing is of major importance. With random dense packing the pressure drop was found to be 1.9 to 2.7 times as high as with random loose arrangement, while the bulk density of the bed varied only by about 20%.

A. BONDI

VISCOSITY INDEX IMPROVER.

U. S. 2,261,577, to A. H. BATCHELDER (STANDARD OIL CO. OF CALIFORNIA), *Natl. Petroleum News*, 36, R-775 (1944).

It is proposed to admix to a liquid a high polymer which is nearly insoluble in the liquid at low temperatures but becomes more and more soluble with increasing temperature. A system results whose viscosity is practically independent of temperature over a wide range, provided the slope of the solubility/temperature curve is equal to the slope of the viscosity/concentration curve of the system. The practical applicability of this unique utilization of rheological principles is still limited to the laboratory due to the necessity of providing special mechanical equipment for the stabilization of the suspension in the low temperature range.

A. BONDI

PLASTICS

EFFECT OF ENVIRONMENTAL CONDITIONS ON MECHANICAL PROPERTIES OF ORGANIC PLASTICS. PART I.

T. S. CARSWELL and H. K. NASON, *Modern Plastics*, 21, 121-6, 158, 160 (1944).

The effects of temperature on organic plastics are reviewed. 157 references.

B.I.P.C.

ELASTO-VISCOUS AND STRESS-OPTICAL PROPERTIES OF COMMERCIAL POLYMERIZED METHYL METHACRYLATE AS A FUNCTION OF TEMPERATURE.

HOWARD A. ROBINSON, RUTH RUGGY, and ELIZABETH SLANTZ, *J. Applied Phys.*, **15**, 343-51 (1944).

The elasto-viscous and stress-optical properties of commercial methyl methacrylate polymer have been measured. Between 66° and 107°C., Young's modulus drops from approximately 400,000 to roughly 200 pounds per square inch and the material behaves like rubber. At 93°C., the viscosity is approximately 10^{12} poise. This drops to 10^9 at 177°C. While the curve is not strictly linear with $1/T$, an activation energy of 30,000 cal. per mole can be deduced for this change. Below 93°C., three rate constants are necessary to describe the delayed elastic process, but two suffice between 93° and 135°C. At 149°C., one such constant is enough, and above this an instantaneous elastic and a viscous flow are sufficient. The change in rate constants with temperature gives rise to elastic activation energies of 9000 to 11,000 cal. per mole. Methyl methacrylate is optically negative but has a stress-optical sensitivity about that of glass. The stress-optical coefficient varies markedly with temperature, showing a sharp maximum at 93.3°C. The stress-optical coefficient is directly proportional to the average relaxation constant. X-ray diffraction patterns show four rings corresponding to spacings of 2.19, 3.07, 6.7, and 14.7 Å. Some slight evidences of crystallinity are shown by diffraction patterns in fibers stretched at 93°C. Fibers stretched at 149°C. show a lesser amount of order, in agreement with the birefringence studies. The second-order transition point occurs at 71.1°C.

MACROMOLECULAR COMPOUNDS. [316]. Microscopic and Electron-microscopic Investigations of Macromolecular Compounds.

MAGDA STAUDINGER, *Chem.-Ztg.*, **67**, 316-20 (1943).

A review of the physical structure and the behavior toward acids and bases of synthetic polymers, such as the polyhydroxymethylenes and polyethylene oxides, which H. Staudinger and coworkers used as model substances for cellulose. The fibrillar structure of polyhydroxymethylene dihydrate crystals which appears on mechanical treatment is shown in micro- and electron microphotographs. The detection of decreasingly finer fibrils with microscopic tools of increasing resolving power—diameters of 0.4 micron under the light microscope, of 0.15 micron under the ultraviolet microscope, and of 10 millimicrons under the electron microscope—makes it seem probable that the basic fibrils are represented by the single macromolecules. Other microphotographs, taken with the light, the ultraviolet, and the electron microscopes, show the effect of treatment of polyhydroxymethylene dihydrate crystals with sulfuric acid and sodium hydroxide. Measurements of the length of the fragments which result from the transverse rupture of the fibrils upon treatment with sodium hydroxide permit an approximate estimation of the D.P. of such fragments. Studies on a polyhomologous series of molten polyethylene oxide show that its fiber-forming ability increases with its D.P. Attempts to demonstrate the existence of this relationship in cellulose fibers by successive degradation

failed, because even the shortest fragments of an extremely degraded fiber, as observed under the electron microscope, still show the original fibrillar structure. In contrast to the attack of the cellulose fibers by acids and oxidizing agents—which causes the chain molecules to be broken along their whole lengths into fragments of lower D.P.—degradation by bacteria proceeds from the ends of the chains toward the center, resulting in complete destruction of the attacked portions. This interpretation seems to explain the fact that cotton, which had been exposed to bacterial attack and which showed signs of thorough physical destruction, possessed a D.P. which hardly differed from that of normal cotton. In cuprammonium hydroxide, the attacked fibers swelled strongly, but failed to show the ballooning phenomenon. The variety of ways in which glucose molecules may arrange themselves in natural compounds is illustrated by reference to glycogen, in which the glucose residues are arranged in all three dimensions, resulting in a giant molecule with a D.P. of 9000 and a diameter of 30 millimicrons. Thus, observation under the electron microscope produced for the first time the image of a well-defined molecule. Photomicrographs and 26 references.

B. I. P. C.

RHEOLOGY OF ORGANIC GLASS. II.

W. SCHEELE, *Kolloid-Z.*, **105**, 209–16 (1943).

Flow curves of various thermoplastic materials are shown with special consideration given to the effect of plasticizer on these materials. Investigations on polyisobutylenes confirm the conclusions drawn in the first part, that the direction constant of the temperature function of the deformation energy decreases with increase in degree of polymerization. 8 references.

R. N. WELTMANN

CHEMICAL CONSTITUTION AND COLLOIDAL STRUCTURE OF FIBER FORMING SYNTHETIC HIGH POLYMERS. II. Molecular Structure, Colloidal Structure and Physical Characteristics of Mesomorphic Chain Polymers.

W. BROSER, K. GOLDSTEIN, and H.-E. KRÜGER, *Kolloid-Z.*, **106**, 187 (1944).

The molecular structures of various polycondensation polymers are discussed in terms of present knowledge of bond lengths, valence angles, atomic radii, etc. The "colloid structures" are then discussed on the basis of the molecular structure, and the physical properties on the basis of the colloidal and molecular structures.

T. ALFREY

PROTEINS

THE STRUCTURAL VISCOSITY AND FOAM FORMING POSSIBILITIES OF HUMAN SALIVAS.

HELLMUTH HOEPFNER, *Kolloid-Z.*, **105**, 216–23 (1943).

Human saliva is measured at extremely low pressures at various time periods of aging. The measurements were carried out with a capillary-type viscometer provided with a special attachment to permit the measurement to be made at extremely low pressures. Saliva shows structural viscosity even after 24 hours of aging, though it changes chemically during this time. At the

lowest pressures the apparent viscosity of saliva is much higher than that of a 20% solution of glycerin, only to decrease to a viscosity between that of this glycerin solution and water on increasing the pressure. Similar curves are obtained for fresh saliva and saliva aged 6 and 24 hours. The authors find that the fresh saliva shows yield value in addition to structural viscosity. The observed data for fresh saliva obey the equation of Ostwald and de Waele. For aged saliva this equation changes to the Bingham-Scott Blair equation. The foaming ability of human saliva is very high for a fresh sample, but decreases fast on aging. Height-time curves are measured to show the foaming ability of fresh and aged saliva compared with that of other foam-forming materials.

R. N. WELTMANN

SOLUTIONS

VISCOSITY OF HYDROGEN FLUORIDE.

J. H. SIMONS and RICHARD D. DRESDNER, *J. Am. Chem. Soc.*, **66**, 1070 (1944).

The measurement of the viscosities of pure hydrogen fluoride, commercial hydrogen fluoride, and hydrogen fluoride containing a small amount of ethyl alcohol was accomplished by means of a viscometer of special design. In the range -10° to -70°C. , hydrogen fluoride has a low viscosity comparable with that of ethyl ether, and is markedly affected by small amounts of certain impurities.

C. K. BUMP

RELATIVE VISCOSITY OF AQUEOUS SOLUTIONS OF SULFAMIC ACID AND OF SOME OF ITS SALTS AT 25°C.

A. F. SCHMELZLE and J. E. WESTFALL, *J. Phys. Chem.*, **48**, 165 (1944).

Schmelzle and Westfall have determined the relative viscosity and density of aqueous solutions of sulfamic acid and its NH_4 , Ba, Ca, and Mg salts. The concentrations of the solutions varied up to the point of saturation. The Jones and Dole equation for fluidities applies for solutions to one normal while the Root equation for densities applies over the concentration range studied.

VISCOSITY OF AQUEOUS SOLUTIONS OF ELECTROLYTES AS A FUNCTION OF THE CONCENTRATION. VIII. Potassium Ferricyanide.

GRINNELL JONES and SCHUYLER M. CHRISTIAN, *J. Am. Chem. Soc.*, **66**, 1017 (1944).

As an extension of previous work in the field of viscosity of aqueous solutions, precise measurements were made of the density and viscosity of aqueous solutions of potassium ferricyanide at various concentrations. The data for density may be expressed with an average deviation of only 0.0023% by the equations:

$$d_4^{25} = 0.99707_4 + 0.181448 c - 0.0204495 c^{3/2}$$

$$d_4^0 = 0.99987_0 + 0.193367 c - 0.0204495 c^{3/2}$$

The data for viscosity may be expressed by the equations:

$$\eta_{25^{\circ}\text{C.}} = 1 + 0.0244\sqrt{c} + 0.10785 c + 0.13262 c^2$$

(Av. dev. = 0.000043)

$$\eta_{0^{\circ}\text{C.}} = 1 + 0.02113\sqrt{c} - 0.18133c + 0.35368c^2$$

(Av. dev. = 0.00003)

It is interesting to note that the viscosity-concentration curve at 0°C. has both a maximum and a minimum. The results indicate that the formula of Falkenhagen and Vernon correctly evaluates the influence of valence type and of the temperature.

D. TELFAIR

VISCOSITY MEASUREMENTS OF SUGAR AND SODIUM PHOSPHATE SOLUTIONS IN WATER.

B. ROSSMANN and E. KAYSER, *Kolloid-Z.*, **106**, 36-39 (1944).

The viscosities of sugar solutions with the addition of various amounts of sodium phosphate are measured on a Höppler viscometer. At low concentrations (0-6% sugar and 0-1.2% phosphate), the viscosity is found to increase linearly with concentration, but it is assumed that at higher concentrations the viscosity increases faster than the concentration. An equation is set up which is analogous to the Einstein equation for dilute solutions. The observed relationships between the refractive index, viscosity, and density are shown to confirm the equation obtained by Pulvermacher. 11 references. R. N. WELTMANN

VISCOSITIES OF PECTIN SOLUTIONS.

H. S. OWENS, H. LOTZKAR, R. C. MERRILL, and M. PETERSON, *J. Am. Chem. Soc.*, **66**, 1178 (1944).

The effects on concentration of the presence of sodium chloride and urea, and of temperature on the viscosity of aqueous pectin solutions are reported. The viscosity varies with concentration in a manner similar to that of other ionizable salts. It increases in dilute solution as the pH is changed to a maximum at about 6 and is reduced by the addition of acid or sodium chloride. Above 0.5% concentration, pH has little effect in the range 1 to 7. Urea has little effect up to 0.5 molal concentration. Temperature in the range 0° to 50°C. has little effect on dilute pectin solutions. It is believed that calculated values for the intrinsic viscosity may be related to molecular weights. A tentative hypothesis to explain the results has been proposed.

C. K. BUMP

THEORY

RATE OF SEDIMENTATION; NONFLOCCULATED SUSPENSIONS OF UNIFORM SPHERES.

HAROLD H. STEINOUR, *Ind. Eng. Chem.*, **36**, 618-24 (1944).

As an initial step in developing a more complete understanding of sedimentation in concentrated suspensions of fine powders, a study is presented of sedimentation in a simple system, under conditions of laminar flow. The effect of concentration on the rate of fall of uniform well-dispersed spheres is investigated both theoretically and experimentally. Tests with suspensions of tapioca particles in oil provide empirical solutions of functions of concentration left undetermined by the theoretical analysis. Tests with fairly uniform microscopic glass spheres support the conclusions drawn from the tests with the larger tapioca particles. 23 references.

B.I.P.C.

SOLUTION OF SOME PROBLEMS OF VISCOUS FLOW.

G. GREEN, *Phil. Mag.*, **35**, 250-62 (1944).

Detailed mathematical analysis is made of a number of problems in viscous flow within certain specified boundary conditions. Flow (*a*) within converging plane walls, (*b*) with hyperbolic boundaries, and (*c*) into a parallel channel, are discussed. 7 references. S. Z.

LONGITUDINAL SCATTERING OF INFRARED RADIATION AND MOLECULAR WEIGHT OF HIGH- AND LOW-MOLECULAR SUBSTANCES.

W. W. LEPESCHKIN, *Kolloid-Z.*, **105**, 205 (1943).

The principle advanced for high-molecular substances—that the longitudinal scattering (Plotnikov effect) of infrared rays is proportional to the cube root of the molecular weight of the scattering substance—is only valid for low-molecular homologous substances, while for other low-molecular substances the scattering depends not only on the molecular weight but on the molecular structure. The presence of hydroxyl groups and even more carboxyl groups promotes the scattering; consequently, the ratio of scattering in a high-molecular weight substance to that in a low-molecular weight substance, the hydroxyl and carboxyl included, is smaller than the ratio of the cube roots of the molecular weight, and the structure factor is greater than 1. This factor is about 1.38 for sugars, 1.43 for citric acid, and 1.6 for a decomposition product of gelatin. It is considered as a practical rule, that the scattering of such substances by their comparison with that of a high-molecular substance is proportional to the fourth root of the molecular weight. This rule affords the possibility of determining the molecular weight of low-molecular decomposition products of proteins. T. BOYD

THE MIXTURE LAW FOR VISCOSITY.

F. KOTTLER, *J. Phys. Chem.*, **48**, 77 (1944).

An expression giving the viscosity of a mixture of two nonassociating liquids as a function of the viscosities of the pure components is derived. This derivation is based on the following assumptions: (1) Viscosity may be described as a function of volume multiplied by an exponential function of the temperature. (2) That portion of the total free energy which represents the energy of activation for the unit process of flow behaves as the total free energy, and is therefore additive for a mixture. The empirical law of Bachinskii is used for the form of the relation assumed in (1), and the derivation of the expression for mixtures is carried through on the basis of Bachinskii's law. An earlier paper by the same author shows good agreement with experiment for five non-associating liquid mixtures. D. TELFAIR

RELATION BETWEEN VISCOSITY AND MOLECULAR WEIGHT IN MACROMOLECULAR SOLUTIONS.

W. O. OSTWALD (Leipzig), *Kolloid-Z.*, **106**, 1-22 (1944).

Numerous experimental curves collected from the literature are reproduced illustrating the viscosity of macromolecular materials as a function of the molecular weight. To cover all the various shapes of curves obtained

experimentally, two basic curves are shown: the S curve, discussed by the author in 1935, and the double S curve consisting of two S parts. Possible geometric variations of these basic curves are developed for most of which experimental evidence is cited. The Staudinger equation giving a linear relationship between viscosity and molecular weight is shown to be only one limiting case of the basic curves. Also Husemann's horizontal line (no change in viscosity with increase in molecular weight) is an exception and is shown to be part of the S curve. The determination of molecular weights by viscosity determinations does not seem possible because of the numerous variations of the viscosity-molecular weight function. It is shown that a viscosity decrease instead of increase is possible when macromolecular materials are dissolved in a solvent, a case which can also be covered by a geometrical variation of the S or SS curve. A short survey is made of the literature on the mathematical equations which might possibly fit the S or SS curve or parts of these curves.

R. N. WELTMANN

UNCURLING OF CHAIN MOLECULES IN STREAMING SOLUTIONS.

W. KUHN and H. KUHN, *Helv. Chim. Acta*, **26**, 1394-1465 (1943).

If it is desired to treat quantitatively the disentanglement of curled-up chain molecules in dilute solutions it is necessary to distinguish two extreme cases. One is materialized if the coiled-up molecule represents a comparatively open structure through which the solvent can flow more or less freely (particle permitting comparatively free through-passage of the solvent). The other is represented by a strongly entangled snarl, in the random loops of which a large amount of solvent is immobilized (particle not permitting free through-passage of the solvent). The first type shall be termed "solvent-permeable" and the other, "solvent-impermeable." Experimentally, a distinction between these two limiting cases can be made: (a) by observing the sedimentation velocity of fractions of a given high polymer in the ultracentrifuge, and (b) by measuring the "free diffusion" constants of the same fraction. The sedimentation constants of solvent-permeable molecules is independent of the molecular weight of the fraction to which the molecule belongs, while in the case of solvent impermeability the sedimentation constant increases with the square root of the molecular weight. On the other hand, the diffusion constant of solvent-permeable molecules is inversely proportional to the molecular weight, while it is inversely proportional to the square root for solvent-impermeable particles.

$$S \text{ (solvent permeable)} \sim M^0$$

$$S \text{ (solvent impermeable)} \sim M^{1/2}$$

$$D \text{ (solvent permeable)} \sim M^{-1}$$

$$D \text{ (solvent impermeable)} \sim M^{-1/2}$$

Practically complete solvent permeability must be expected: (a) if the polymerization degree is low, and (b) if the chain has bulky and geometrically odd substituents. Practically complete immobilization can be expected at high degrees of polymerization and in the presence of highly flexible chains which allow a dense packing. An analysis is carried out of the various factors which contribute to the motion of a particle and to its orientation and shape; these factors are: (1) the hydrodynamic forces, (2) the kinetic elasticity of the particle, and (3) the rotational Brownian movement. The amount of birefringence of flow is given by the product of a constant times the degree of poly-

merization; the orientation of the birefringence is at 45° as long as the flow is slow, and with increasing rate of shear, moves to smaller and smaller angles with the direction of flow. At small flow rates, the ratio of birefringence and orientation proves to be inversely proportional to the degree of polymerization. Predictions are also possible about a dichroism of flow which is expected to exist if the chain molecules bear rigid elements with anisotropic chromophoric groups. The partial disentanglement of the macromolecules in the streaming solution also contributes to the viscosity characteristics of the system. For complete solvent permeation and small rates of shear, the intrinsic viscosity becomes directly proportional to the molecular weight (Staudinger's rule), while this is no longer true as soon as part of the molecules are not completely permeated by the solvent, particularly not in the range of higher molecular weights. Finally, the authors discuss characterizing a polymer in dilute solution by combined measurement of viscosity, flow birefringence, and sedimentation.

H. MARK

ON THE THEORY OF THE VISCOSITY OF SOLUTIONS OF MACROMOLECULAR MATERIALS. I. General Considerations.

P. H. HERMANS, J. J. HERMANS, and D. VERMAAS (Utrecht, Holland), *Kolloid-Z.*, **105**, 199-204 (1943).

Various explanations are given for the behavior of the viscosity of macromolecular materials. The relatively fast increase of the viscosity of such materials with increasing concentration, according to the authors, is due to the interaction of the closely packed micelles. The interaction can be divided into two main groups: (a) currents of hydrodynamic nature; (b) forces acting between the micelles. Time effects, which have been observed frequently in such systems, can be explained by an equilibrium of association, which is reached at finite velocity, the equilibrium being obtained after a certain time period. The steepness of the viscosity increase depends on the molecular weight and shape and also on the character of the solute and solvent. The increase in viscosity with concentration is faster in so-called good solvents than it is in poorer ones. The older theories of the viscosity of very dilute suspensions assumed undeformable particles or molecules. To the authors it seems much more probable that the micelles are continuously deformed by shear and at the same time tend to return to their most probable shape. The product of shear modulus and relaxation time will be shown in a later paper to contribute to the viscosity in such a way that it justifies quantitative observations.

R. N. WELTMANN

ON THE THEORY OF THE VISCOSITY OF SOLUTIONS OF MACROMOLECULAR MATERIALS. II. A Simple Theory of the Viscosity of Extremely Dilute Macromolecular Solutions on the Basis of the Deformation of the Molecule Shape.

J. J. HERMANS (Utrecht, Holland), *Kolloid-Z.*, **106**, 22-29 (1944).

The macromolecules in solution are considered to be curled up and to undergo a deformation when being sheared. Then, the shear modulus, being responsible for the deformation, can be calculated according to Kuhn's statistical theory. The molecules need a certain time, the time of relaxation, to return to their statistically most probable shape. The product of shear modulus and relaxation time is considered to be the viscosity contribution of the mole-

cules. This assumption leads to the Staudinger viscosity-molecular weight function. From it the increase of viscosity can be calculated quantitatively. The final equation contains a factor which depends on the degree of stretching of the molecules. The degree of stretching thus calculated seems to be reasonable in all cases. From the final equation it is believed to be possible to find the degree of stretching as a function of solvent and temperature. The author emphasizes that he is not satisfied with the experimental proof of the Staudinger equation. But he is convinced that the assumption of a curled-up molecule changing its shape on shear will lead to a better understanding of the viscosity behavior of macromolecular materials.

R. N. WELTMANN

CONTRIBUTION TO THE THEORY OF THE VISCOSITY OF SOLUTIONS OF HIGH MOLECULAR WEIGHT SUBSTANCES. III. A General Consideration of the Dependence of the Viscosity of Solutions of High Molecular Weight Substances on the Concentration.

J. J. HERMANS, *Kolloid-Z.*, **106**, 95 (1944).

Hermans has discussed the degree of cross linking in high-molecular substances with respect to the viscosity of solutions of high polymers. An attempt has been made to come to some quantitative principle relative to cross linking in high polymers and the properties of their solutions which depend upon such structure.

THE RELATION BETWEEN TENSILE STRESS, STRAIN DOUBLE REFRACTION, AND DEFORMATION MECHANISM OF RUBBERLIKE SUBSTANCES.

J. J. HERMANS, *Kolloid-Z.*, **103**, 210-21 (1943).

The early part of this paper is largely a review of the well-known theoretical work on the long-range elasticity of rubberlike substances. The most interesting sections of the paper are those numbered V and VI. *Part V* deals with the optical anisotropy which accompanies strain. The treatment presented is far from being a final definitive work, but, as far as it goes, is sound. Hermans starts from the assumption that each link of the polymer chain can be characterized by two polarizabilities—parallel and perpendicular to the bond direction. The double refraction of the macroscopic sample is then correlated with the distribution among angular orientations of the various links. *Part VI* is an ambitious attempt to solve the question of the rate of attainment of elastic equilibrium. In the unstrained state, the second chain end is distributed about the first according to the well-known distribution law:

$$\psi_0(x, y, z) = A e^{-\mu^2 r^2}$$

A different distribution of chain end separations, ψ_1 , will in general correspond to a finite strain. Hermans considers that a given chain end distribution is subject to the following two "driving forces," which tend to change it to some other distribution: the "diffusion force," equal to $-kT \text{ grad} (\ln \psi)$, and the force $-2kT \mu^2 \vec{r}$, which is connected with the entropy decrease that results when the chains are widely separated. If λ is a viscosity term which measures the resistance to relative motion of two chain ends, then Hermans proposes the following equation:

$$\lambda \frac{\vec{u}}{u} = -kT \text{grad} (\ln \psi) - 2 k t \mu^2 \frac{\vec{r}}{r}$$

where $\frac{\vec{u}}{u}$ is the velocity of the second chain end. Eventually, Hermans proposes the following differential equation:

$$\frac{1}{D} \frac{\partial \psi}{\partial t} = \Delta \psi + 2 \mu^2 r \frac{\partial \psi}{\partial t} + 2 \mu^2 \psi$$

where D is a diffusion constant connected with the viscous resistance constant λ ($D = k t / \lambda$). The author then discusses the solutions to this differential equation. In several important respects this approach is a decided oversimplification of the problem. However, it is extremely interesting and may be an important step toward an extension of the kinetic theory of high elasticity into the realm of nonequilibrium behavior.

T. ALFREY

STRUCTURE MECHANICS OF ELASTOVISCOUS CONTINUA. IX. The Question of Hysteresis in Rheological Systems.

H. UMSTÄTTER (Ploesti, Rumania), *Kolloid-Z.*, **105**, 182-90 (1943).

From data of Philippoff on a solution of Oppanol (isobutylene polymer) in decalin, it is shown that the logarithm of the velocity gradient plotted against the logarithm of the tangential pressure results in a slight hysteresis loop in the region of medium pressures. At low and high pressures no hysteresis loop exists, and only one curve results; an S-shaped hysteresis loop is thus formed. Such a curve indicates that the viscosity approaches a constant value at extreme low and extreme high pressures. The loop in the middle range of pressures indicates the time dependency of the viscosity. For further investigation the Maxwell shear equation is used. Space diagrams for shearing stress, time, and velocity under six different conditions are drawn. The Maxwell equation is:

$$F = E \tau ds/dt + C e^{-t/\tau}$$

where F = shearing stress, E = shear elasticity, τ = time of relaxation, ds/dt = rate of shear, C = a constant, and t = time. The conditions for which the space diagrams are given are: (1) The velocity increases linearly with time. (2) The shearing stress is constant. (3) The shearing stress increases as a function of time. (4) The velocity first increases with time and then decreases again. (5) The velocity changes sinusoidally with time starting with high velocities. (6) The shearing stress changes sinusoidally. All these diagrams are only valid for true liquids, where C is a function of the rate of shear and the rate of shear increases linearly with the shearing stress. The author mentions that it is possible that C might be partly independent of the rate of shear. Then, for $ds/dt = 0$, the shearing stress would still have a finite value. This, the author claims, would be the case for thixotropic materials which, however, are not discussed in this paper. A comparison is drawn between magnetic hysteresis and the hysteresis loop of the flow curve, thixotropy being compared to the residual magnetism and yield value to the coercive force. The ascending branch of a magnetic hysteresis loop is compared to plasticity, the part of the descending branch of positive magnetic force to structural viscosity, and the other part of the descending branch to rheopexy. The axes on the rheological

hysteresis loop are the tangential pressure as abscissa and the fluidity as ordinate. The following equation relating shearing stress, F , and rate of shear, S , is integrated from Newton's equation:

$$F = \frac{E S}{\ln t/\tau}$$

It is analyzed for various flow systems with special consideration to relaxation times of the materials. Both equations, Maxwell's and Newton's, have limitations. The Maxwell equation is only valid for systems showing a continued deformation with constant rate of shear, while the Newton equation is only valid when the deformation times are of the same magnitude as the relaxation times. According to the author three basic qualities of matter exist, shear elasticity, relaxation time, and layer thickness, which determine essentially most properties, as, for instance, viscosity, hardness, ductility, plasticity, elasticity, consistency, and stickiness.

R. N. WELTMANN

MECHANICS OF VISCOELASTIC CONTINUA. IX. The Question of Hysteresis in Rheological Systems.

H. UMSTÄTTER, *Kolloid-Z.*, **105**, 182-90 (1943).

This paper attempts to provide a mathematical treatment of viscoelastic behavior of a Maxwellian material (exhibiting flow superimposed upon elasticity) to a number of experimental conditions. Unfortunately, the reasoning is based upon a completely erroneous assumption. In a Maxwellian material, the shearing stress $F(t)$, the shearing strain $s(t)$, and time (t) are interrelated by the differential equation:

$$\frac{ds}{dt} = \frac{1}{E} \frac{dF}{dt} + \frac{1}{\eta} F \quad (1)$$

where E and η are the shear modulus and the viscosity, respectively. If $F(t)$ is defined by a specific function, then the above equation can be solved for the strain as a function of time, and if $s(t)$ is known we can solve for $F(t)$. One special case is that of constant rate of strain, where $ds/dt = C$. For this case, equation (1) can be solved to give the following stress function:

$$F(t) = \eta C + A e^{-Et/\eta} \quad (2)$$

where A is an arbitrary constant. This equation, of course, applies only when the rate of straining is constant. In spite of this fact, Umstätter writes the form:

$$F = \eta \frac{ds}{dt} + A e^{-Et/\eta} \quad (3)$$

and applies (3) even where ds/dt is not a constant, but is any arbitrary function. The fundamental differential equation (1) is not even mentioned; instead, (3) is directly introduced as "the Maxwell equation." The author then applies (3) to a number of special cases: constant acceleration of strain, constant stress, sinusoidal stress variation, sinusoidal strain variation, etc. The results so obtained are represented in the form of beautiful three-dimensional diagrams. The practical value of these is somewhat reduced, however, by the fact that they are incorrect.

T. ALFREY

A MOLECULAR THEORY OF THE VISCOELASTIC BEHAVIOR OF AN AMORPHOUS LINEAR POLYMER.

T. ALFREY, *J. Chem. Phys.*, **12**, 9 (1944).

The author discusses briefly the deficiencies of the kinetic theory of long-chain elasticity and points out that the emphasis which it places upon chain end separation renders it unacceptable with reference to linear polymers. The need for a molecular theory which will describe the behavior of a linear polymer during the establishment of elastic equilibrium is noted, and such a theory is proposed. From a consideration of the linear polymer as a statistical distribution of kinks and bends, the mathematical manipulation leads to the behavior empirically attributed to amorphous polymers, that is, "a distribution of elastic compliances over a wide range of retardation times." The author observes that the theory does not hold well for short retardation times and suggests further work on the basic equations of high elasticity. R. H. KELSEY

EFFECT OF DEFORMATION ON THE SWELLING CAPACITY OF RUBBER.

PAUL J. FLORY and JOHN J. REHNER, *J. Chem. Phys.*, **12**, 10 (1944).

From an expression of the entropy change in passing from the unstressed, unswollen, to the stretched, swollen, state, the authors derive an expression which predicts that the relative volume of stretched rubber in equilibrium with a swelling agent should be equal to the square root of its relative stretched length, in equilibrium with the swelling agent. Experimental evidence is presented in support of this conclusion. R. H. KELSEY

MOLECULAR STRUCTURE AND RUBBER ELASTICITY.

H. MARK, *Rubber Age*, **55**, 367 (1944).

A general picture is given of the structure of liquids, glasses, solids, and high polymers. The formation of rubbery solids is explained upon the basis of long-range entanglement of generally disordered chain molecules. Two types of Brownian movement are discussed and their relation to "snap" and "creep" of rubbery substances is described. The problems of flow and relaxation under stress are mentioned; methods of providing stable structures by vulcanization, by active fillers and by strongly cohesive molecular groups are given. The rubbery qualities of several types of long-chain structure are compared. R. H. KELSEY

