

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Viscous Flow of Large Molecules

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A. General Theory of Viscosity.—It was shown by Eyring¹ that the viscosity of a liquid is given by

$$\eta = \frac{2\lambda_1 h f}{\lambda k T} e^{-\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT} \sinh \frac{f\lambda\lambda_2\lambda_3}{2kT} \quad (1)$$

where η = viscosity; h = Planck's constant; λ_1 = distance between moving layers of molecules, λ_2, λ_3 = dimensions of unit of flow in the direction of flow and perpendicular to the direction of flow (the directions of λ_2 and λ_3 both being perpendicular to that of λ_1); λ is the distance moved by each unit of flow; f is the shear force per unit of area; k is the Boltzmann constant, T the absolute temperature, R is the gas constant per mole, ΔS^\ddagger is the entropy of the unit of flow in the activated state over and above that in the normal state, ΔH^\ddagger is the heat of activation of the unit of flow.

When $f \ll \frac{2kT}{\lambda\lambda_2\lambda_3}$, $\sinh \frac{f\lambda\lambda_2\lambda_3}{2kT} \approx \frac{f\lambda\lambda_2\lambda_3}{2kT}$ and (1) becomes

$$\eta = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} e^{-\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT} \quad (2)$$

so that the viscosity is independent of the shearing force (Newtonian flow). The quantity $\lambda_2\lambda_3\lambda^2/\lambda_1$ is probably of the order of the volume of the unit of flow. If the volume per mole of this unit is V , then $\lambda_2\lambda_3\lambda^2/\lambda_1 \approx V/N$ and (2) becomes

$$\eta = Nh/V e^{-\Delta S^\ddagger/R} e^{\Delta H^\ddagger/RT} \quad (3)$$

Now, it has been found² that there is a rather intimate relation between ΔH^\ddagger and ΔH of vaporization for substances made up of small molecules (*i. e.*, where the unit of flow is the molecule). Specifically, the ratio $\Delta H_{\text{vap}}/\Delta H^\ddagger$ is found to be ~ 3 for spherical molecules and ~ 4 for other molecules. Since we can usually make a fair guess as to the heat of vaporization of a group of atoms of a given size and constitution, we can, knowing ΔH^\ddagger , form some idea of the size of the unit of flow by using this relationship. We shall make use of this later on.

The significance of this ratio seems to be that in order to flow, a hole of a certain size must be available into which the given unit of flow can

move. The energy of formation of a hole the size of a molecule is ΔH_{vap} , while the unit of flow apparently only needs in general a hole requiring a quarter as much energy of formation.

The relationship between holes and viscosity is made more direct by means of a relationship discovered empirically by Batschinski.³ If V is the specific volume of the liquid and ϕ ($= 1/\eta$) is its fluidity, then Batschinski found that

$$(V - V_0) = R\phi \quad (4)$$

V_0 has been identified⁴ with the volume of the unexpanded solid. Now Eyring¹ has shown that as a consequence of the Law of Rectilinear Diameters of Cailletet and Mathias (that the average densities of a liquid and its vapor are approximately the same at all temperatures below the critical point), the expansion of a liquid is largely due to the introduction of holes into the liquid, as opposed to the expansion of the liquid due to increased lattice vibrations at higher temperatures (which accounts for only a minor part of the expansion). Therefore, $V - V_0$ is a measure of the number of holes present in the liquid, and we may say that the fluidity is proportional to the number of holes present in the liquid.

The intimate relationship between number of

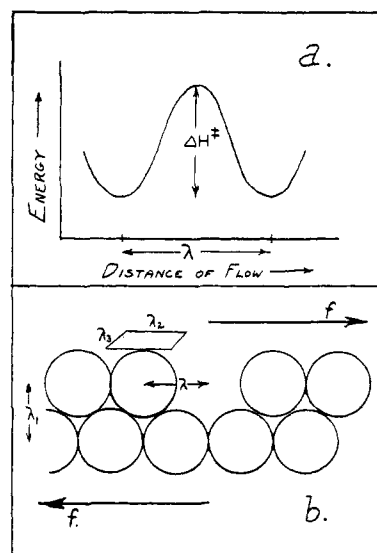


Fig. 1a, b.

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(1) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

(2) R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

(3) A. J. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

(4) R. E. Powell, E. Roseveare and H. Eyring, in preparation.

holes (as measured by the specific volume) and viscosity is made even more apparent by the fact that if a system is subjected to changes of pressure and of temperature in such a way that the volume is held constant, the viscosity remains constant.⁴

A third indication of the relationship between the number of holes and the viscosity is found in the behavior of the viscosity at the melting point. It has been found⁴ that simple substances on melting usually expand in such a way that a definite number of holes are introduced into the liquid. Since the number of holes so introduced is the same for all simple substances, it should be clear that if the viscosity is a function of the number of holes alone, all substances should have the same viscosity at the melting point. This is actually the case, all simple substances for which data are available having a viscosity of about 0.02 poise at the melting point.

B. Viscosity as a Function of Increasing Chain Length for Chains up to 30 Atoms in Length.—In order to gain some insight into the mechanism of flow of very large molecules, it will be instructive to study the behavior of the viscosities of normal hydrocarbons as the chain length is increased.

(1) **Activation Energy of Flow as a Function of Chain Length.**⁵—In Fig. 2 are plotted a fourth

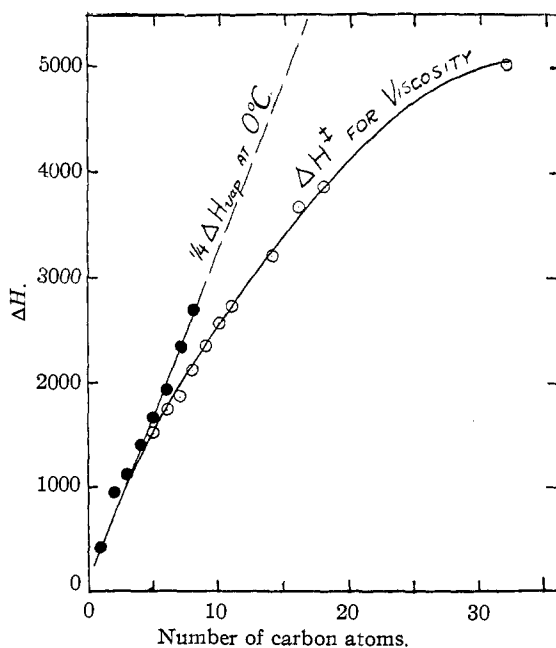


Fig. 2.

(5) The data used in this section and the next are from "Landolt-Börnstein's Tabellen," "International Critical Tables" and Bridgman's "Physics of High Pressure," The Macmillan Co., New York, N. Y.

of the heats of vaporization and the heats of activation for viscous flow as a function of chain length for normal paraffins. The curve for heats of vaporization has been extrapolated as a straight line through the value for hydrocarbons up to octane. Values for chains longer than about eight carbon atoms were not used because their tendency to roll into a ball in the vapor (due to intra-molecular van der Waals forces) will make the heat of vaporization a poor measure of the energy required to make a hole the size of a molecule in the liquid for longer chains. A straight line was used in the extrapolation because we expect that the energy required to make a hole the size of a normal paraffin will increase linearly with the chain length. It will be noted that as the molecule gets longer, ΔH^\ddagger for viscous flow increases less rapidly than $\frac{1}{4}\Delta H_{\text{vap}}$, and that there is a decided tendency for ΔH^\ddagger to level off as the

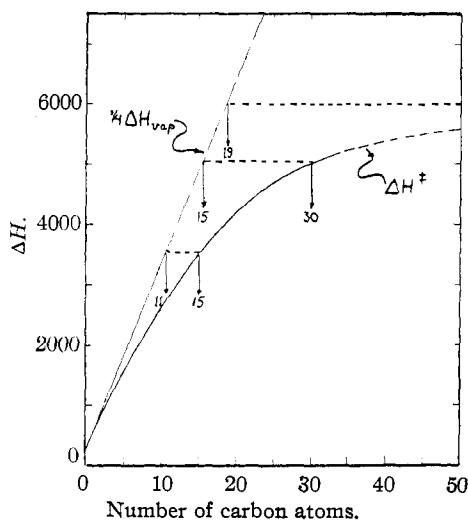


Fig. 3a.

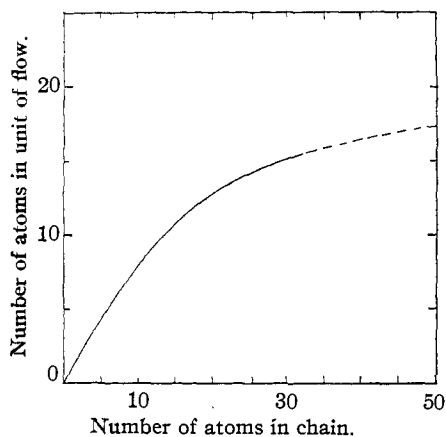


Fig. 3b.

chain increases in length to thirty carbon atoms. This means that the hole required for the molecule to move becomes smaller relative to the size of the molecule as the molecule gets larger. That is, as the molecule gets larger, it no longer moves as a unit, and if the tendency for ΔH^\ddagger to become independent of chain length is real, we can say that when a chain becomes sufficiently large, it moves in units of a fixed size which is independent of the size of the molecule. If these units, in order to move, still require a hole costing a quarter of the heat of vaporization of a molecule of the same size as the unit, we can estimate the sizes of these units as follows. In Fig. 3a we duplicate Fig. 2, but carry out what seems to be a reasonable extrapolation of ΔH^\ddagger . Now, in order to find the size of the unit of flow in a chain of length n , we merely draw a line parallel to the horizontal axis, and the point at which this intersects the $\Delta H_{\text{vap}}/4$ curve will give some idea of the average size of the unit of flow. In Fig. 3b is given a plot of total chain length against the average chain length of the unit of flow, and it is seen that the unit of flow in very large hydrocarbon chains is probably twenty or twenty-five carbon atoms in length, on the average. This corresponds to an activation energy of 6-7 kcal. for flow.

(2) **Further Details on the Viscosities of n -Paraffin.** (a) **Fluidity and Specific Volume.**—When the fluidity of homologous normal paraffins is plotted against their specific volume it is found that the resulting curves for different hydrocarbons fall on top of one another (Fig. 4), at least up to lengths of fourteen carbon atoms. Beyond C_{14} , however, the hydrocarbons tend to act less fluid than they would be if they lay on top of the curves for the smaller chains. The explanation for the dependence of fluidity on specific volume is apparently as follows: Powell, Roseveare and Eyring have shown⁴ that the number of holes in a mole of liquid is equal to $N \frac{V - V_0}{V_0} r$, and we have seen that the fluidity is a function of the num-

ber of holes which are present. Therefore

$$N \frac{V - V_0}{V_0} r = k\phi \quad (5)$$

Here, $r \sim 6$ for paraffins, V is the molar volume, V_0 is the volume the liquid would have if no holes were present, k is constant for all substances whose flow depends only on the number of holes which are present, N is Avogadro's number, and ϕ is the fluidity. V_0 may be taken as the mole volume of the solid, and it seems reasonable that the molar volumes of solid hydrocarbons are quite closely proportional to the molecular weight of the hydrocarbons. That is, $V_0 = Mv_0$, where v_0 is the specific volume of a solid hydrocarbon and

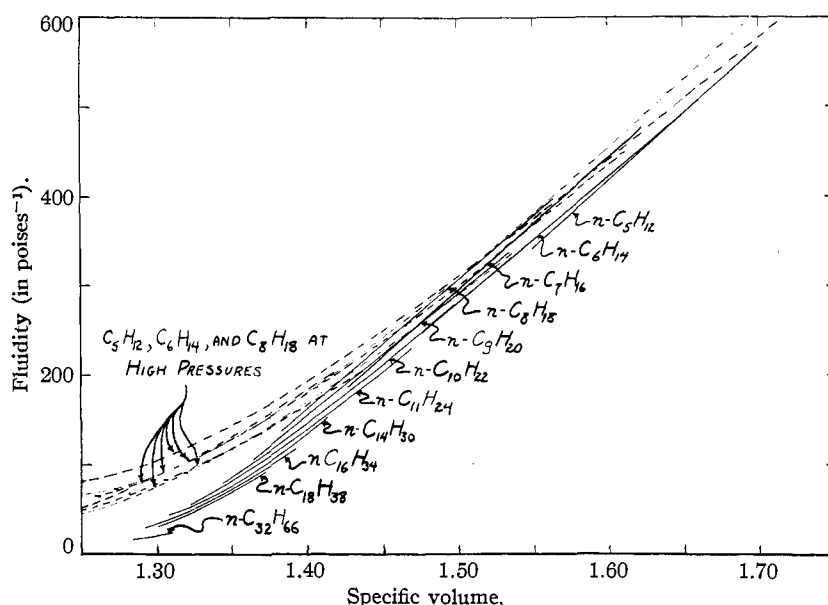


Fig. 4.

is a constant and M is the molecular weight. By definition $V = Mv$, where v is the specific volume. Therefore, we may write (5) as

$$(v - v_0)/v_0 = v/v_0 - 1 = k/Nr\phi \quad (6)$$

and we see that as long as the fluidities of hydrocarbons only depend on the number of holes which are present, the relationship shown by the smaller chains in Fig. 4 should be true. The fact that chains with more than about fourteen carbon atoms in them do not obey the relationship so well indicates that something in addition to the number of holes is becoming important here, and since the curves fall below those for the shorter chains, this factor is acting to *reduce* the fluidity.

The effect which lengthening of chains has in reducing the fluidity is also shown when we compare the fluidities of short chains at high pressures

with those of long chains having the same specific volumes (Fig. 4). Here, however, the effect seems to become noticeable somewhat sooner than at a chain length of fourteen atoms.

(b) **Viscosities at the Melting Point.**—It has been mentioned above that at the melting point, all substances whose fluidities depend on the number of holes which are present have a viscosity of 0.02 poise.

By extrapolating the $\log \eta$ vs. $1/T$ curves for the normal hydrocarbons to their melting points, we can use this relationship to test the importance of holes in viscous flow as a function of chain length. The results are given in Table I, and it is seen at about C_{14} , there begins a definite increase in viscosity at the melting point, indicating that something beside the requirement of holes is acting to impede flow.

TABLE I

Substance	At m. p.	Substance	At m. p.
Pentane	((0.0384)) ^a	Undecane	0.0246
Hexane	(.0197) ^b	Tetradecane	.0285
Heptane	(.0269) ^b	Hexadecane	.0331
Octane	.0178	Octadecane	.0359
Nonane	.0294	Dotriacontane	.0671
Decane	.0210		

^a Very uncertain extrapolation. ^b Uncertain extrapolation.

(3) **Conclusions Concerning Normal Paraffins.**—From this study of the viscosities of homologous normal paraffins, we conclude, then, that as chains increase in length they cease to flow as whole molecules, but flow in segments. The activation energy of flow seems to become independent of chain length. For paraffins, the segments which flow are probably of the order of 20–25 carbon atoms in length while the heat of activation for a segment is probably around 6–7 kcal. Furthermore, from the behavior of the fluidity with volume and at the melting point, there is some evidence that a factor other than the requirement of holes for flow is influencing the flow of these molecules as they get longer than about fourteen atoms in length.

C. Viscosities of Molecules Longer than Thirty Atoms.—Whereas in the previous section we have studied the viscosities of pure substances with a definite chain length, when we seek to extend our observations to longer molecules we can no longer deal with substances having a clearly defined chain length, but must speak of average chain lengths. The seriousness of the limitation

thus imposed depends upon the sharpness of the distribution about the mean length, and it is obviously desirable to keep the range of variation of lengths as narrow as possible. Unfortunately, this is a rather difficult condition to meet in practice.

It is probably safe to say that whenever, in the absence of small molecules, large molecules flow according to equation (1), they flow through the successive movements of segments rather than as entire molecules. This was indicated by the behavior of long hydrocarbon molecules, above. Furthermore, it is the way one would expect them to flow, since the energy required to furnish a hole large enough to permit an entire macromolecule to move would be excessive if it had to be provided in one lump. Finally there is definite evidence that they do flow as segments, since (a) the observed energies of activation of flow are rather low (about 10 kcal. usually) and (b) Flory⁶ has observed that the temperature coefficients of the viscosities of several condensation polymers are independent of the molecular weight of the polymer.

(1) **Sizes of Moving Segments in Some Actual Long Chain Molecules.**—We have shown above how, from the heat of vaporization and from the heat of activation for viscous flow, it is possible to calculate the average size of the units whose movements permit the flow of liquids. This method has been utilized to calculate the size of the unit of flow in μ sulfur ("plastic" sulfur) and in rubber by Ewell and Eyring.^{2,7} These calculations will be reviewed here, and they will be extended to the substances treated by Flory.

Smallwood⁸ has analyzed data of Mooney⁹ on the viscosity of rubber in terms of equation (1). He has found the following values for the constants appearing there

$$\begin{aligned}\lambda_2 \lambda_3 \lambda &= 352,000 \text{ \AA.}^3 \text{ per unit of flow}^{10} \\ \Delta E &= 10,200 \text{ cal. per unit of flow} \\ \lambda_1 / \lambda e^{-\Delta S^\ddagger / R} &= 1.31 \times 10^9\end{aligned}$$

If $\lambda_1 \sim \lambda$, which is certainly true as far as orders of magnitude go (no more accurate assumption is needed here), then $\Delta S^\ddagger = -42$ cal. per degree.

(6) P. J. Flory, *THIS JOURNAL*, **62**, 1057 (1940).

(7) R. H. Ewell, *J. Applied Phys.*, **9**, 252 (1938).

(8) H. M. Smallwood, *ibid.*, **8**, 505 (1937).

(9) M. Mooney, *Physics*, **7**, 413 (1936).

(10) Dr. Smallwood has informed us of a misprint appearing in his paper (ref. 8). His value of b , given as 1.28×10^{-5} on page 508, should have been 1.28×10^{-4} , so that the value of about 3520 \AA.^3 for $\lambda_2 \lambda_3 \lambda$ derived from the former figure and used by Ewell (reference 7) is in error, and the value of $352,000 \text{ \AA.}^3$ as given in Smallwood's paper is correct.

TABLE II

<i>n</i>	Polymer unit	<i>A</i>	<i>B</i>	<i>C</i> = ΔH^\ddagger , cal.
8	—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₆ —CO—	-27.8	0.510	8050
7	—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₄ —CO—	-28.3	.527	8230
6	—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₂ —CO—	-28.9	.516	8550
5	—O—(CH ₂) ₂ —O—(CH ₂) ₂ —O—CO—(CH ₂) ₄ —CO—	-27.8	.457	8400

Rubber is made up of units of isoprene, so that in order to find from the heat of vaporization of a segment (= $4 \times 10,200 = 40,800$ cal.) the size of the segment, we had best see how many isoprene molecules could be vaporized by 40,800 cal. Since the heat of vaporization of isoprene is about 4000 cal./mole, ten isoprene units, or forty chain atoms make up the average segment which causes rubber to flow. We can check this figure against the value of the "viscous volume," $\lambda_2\lambda_3\lambda$, which we should expect for a segment of this size. A chain of forty carbon atoms is about 50 Å. long and the diameter is about 5 Å., while the distance λ through which the segment moves on each jump is probably of the same magnitude as the diameter of the chain. This gives a calculated $\lambda_2\lambda_3\lambda$ of 1250 Å.³ as against an observed 352,000 Å.³ which is a very serious discrepancy for which we can at the moment offer no explanation.

Flory has found that the viscosities of polymers of "weight average chain length" Z_e (Z_w giving the number of atoms in an average chain) are given by

$$\log_e \eta = A/R + (B/R)Z_w^{1/2} + C/RT \quad (7)$$

where R is the gas constant, T is the temperature and A , B and C are constants independent of the temperature. The values of the constants for different types of polymers are given in Table II.

From equation (3) we see that

$$\log_e \eta = \log_e Nh/V - \Delta S^\ddagger/R + \Delta H^\ddagger/RT \quad (8)$$

so that C is the activation energy for the movement of the segments.

In order to calculate the size of the moving segments, we need to know the heat of vaporization of an ester containing one carboxyl group per n

methylene groups, where n is given in Table II (the ether oxygen in diethylene adipate being taken as equivalent to a CH₂ group). These can be fairly closely estimated from the data in Table III. Using these data, we can say that, roughly, when $n = 8$, $\Delta H_{\text{vap.}} = 9.5$ kcal., 7, $\Delta H_{\text{vap.}} = 9.0$ kcal., 6, $\Delta H_{\text{vap.}} = 9.0$ kcal., 5, $\Delta H_{\text{vap.}} = 8.5$ kcal. Using the relationship, $\Delta H_{\text{vap.}} = 4\Delta H^\ddagger$, we can calculate a heat of vaporization for the segment which acts as the unit of flow for these molecules to be:

$$\begin{aligned} \text{for } n = 8 & \quad \Delta H_{\text{vap.}} = 32.3 \text{ kcal.} \\ n = 7 & \quad \Delta H_{\text{vap.}} = 32.9 \text{ kcal.} \\ n = 6 & \quad \Delta H_{\text{vap.}} = 34.2 \text{ kcal.} \\ n = 5 & \quad \Delta H_{\text{vap.}} = 33.6 \text{ kcal.} \end{aligned}$$

This means that on the average the number of atoms in the chain making up the moving segments of the various polymers are as follows:

Polymer unit	Average number of chain atoms per unit of flow
—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₆ CO—	34
—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₄ CO—	33
—O—(CH ₂) ₁₀ —O—CO—(CH ₂) ₂ CO—	30
—O—(CH ₂) ₂ —O—(CH ₂) ₂ —O—CO—(CH ₂) ₄ —CO—	~28

Knowing the number of atoms in a segment we can estimate the value of V in equation (3) and so determine ΔS^\ddagger from A in Table II. On the average, these polymers have a density around unity, and the segment molecular weight is around 500, so $V \cong 500$ cc. per mole of segments. Then from (7) and (8)

$$\begin{aligned} \Delta S^\ddagger &= R \ln Nh/V - A - BZ_w^{1/2} \\ &= -21.2 - A - BZ_w^{1/2} \end{aligned}$$

Since $A = -28$ and $B = 0.5$ for these polymers

$$\Delta S^\ddagger = 6.8 - 0.5Z_w^{1/2} \quad (9)$$

This means that the segment which moves gains 6.8 entropy units on activation less an amount involving the size of the molecule as a whole and which we shall consider in more detail later.

The size of the moving segments in plastic sulfur (high temperature liquid) has been calculated as 36 atoms by Ewell and Eyring from observed activation energy of 18.4 kcal. and the heat of vaporization of 2.05 kcal. per gram atom of plastic sulfur. The peculiar behavior of the viscosity of sulfur with different rates of heating, however,

TABLE III

Substance	No. of methylene groups per —COO—	$\Delta H_{\text{vap.}}$, kcal.
CH ₃ (CH ₂) ₆ COO—CH ₂ CH ₃	9	10
CH ₃ (CH ₂) ₃ COO—(CH ₂) ₂ CH ₃	7	8.8
CH ₃ (CH ₂) ₃ COO—CH ₂ CH ₃	6	10
CH ₃ (CH ₂) ₂ COO—(CH ₂) ₂ CH ₃	6	8.8
CH ₃ CH ₂ COO—(CH ₂) ₃ CH ₃	6	9.3
CH ₃ (CH ₂) ₃ —COO—CH ₃	5	8.1
CH ₃ (CH ₂) ₂ —COO—CH ₂ —CH ₃	5	8.4
CH ₃ CH ₂ —COO—(CH ₂) ₂ —CH ₃	5	8.4
CH ₃ —COO(CH ₂) ₄ —CH ₃	5	8.6

makes it desirable to examine these figures further. Rotinjanz¹¹ found that if viscosities of sulfur are measured while the sample used is being heated, much greater viscosities are observed than if measurements are taken while the sample cools. Furthermore, the addition of very small amounts of foreign materials (*e. g.*, iodine or ammonia) decreases the viscosity very markedly. This leads one to suspect that as plastic sulfur is heated, the chains of sulfur atoms of which it is made are broken down into shorter lengths, and that unless the subsequent cooling is slow, the chains do not recombine into their equilibrium lengths. Small amounts of foreign substances act similarly in breaking chains. Therefore, part of the temperature coefficient of the viscosity is caused by the breaking of chains by heat so that the heat obtained from a $\log \eta$ vs. $1/T$ plot is not a true heat of activation. Something closer to a true heat is probably obtained on cooling the chains, since their lengths change less rapidly on cooling. Activation energies in the neighborhood of 10,000 cal. are found here, although this value is quite uncertain due to its dependence on the rate of cooling and other complicating factors. An activation energy of 10 kcal. would give a unit of flow about 20 atoms in length, which is similar to that found in the hydrocarbons. Such a segment length, with an activation energy of 10 kcal., gives an entropy of activation of -37 cal./degree for flow. A segment length of 36 with an activation energy of 18.4 kcal. gives an entropy of activation of -55 cal./degree. If the entropy of activation of the segment is small, so that the entire entropy of activation is due to a $BZ_w^{1/2}$ term like that in equation (7), and if $B/R = 1/4$ for sulfur as it does for other polymers,¹² then the weight average length of a sulfur chain is calculated as 12,000 atoms, if $\Delta S^\ddagger = -55$, or 5500 atoms if $\Delta S^\ddagger = -37$. These figures are reasonable, but are of course rather uncertain in the light of our assumption.

The entropy of activation of rubber was found to be -42 cal./degree. If, again, the entropy of activation of a segment is small, so that most of this is due to a $BZ^{1/2}$ term, and if $B/R = 1/4$, then the weight average length of a rubber chain is calculated as ~ 7000 atoms, which is again a reasonable figure.

It might be objected that by setting the heat of activation for flow equal to a quarter of the heat of vaporization of a molecule of the same size and nature as the moving segment, we have neglected possible contributions to the

activation energy due to restricted rotation about C-C bonds. Since we have said that separate portions of the molecule move in viscous flow, some articulation about bonds certainly must occur, and since it is known that something like 3 kcal. is required to rotate about a C-C bond, the contribution from this source might be considerable. It would seem, however, that owing to close spacing of the states near the top of the barrier restricting rotation, a relatively large number of bonds are nearly in a position to rotate in their normal state. Furthermore, many of the bonds in an ester probably require much less than 3 kcal. in order that rotation may occur. Hence this heat required for articulation is probably considerably under 3 kcal.

(2) **Dependence of Viscosity on Total Chain Length for Large Molecules.**—We have seen that as normal hydrocarbon chains get longer, their viscosity shows evidence of increasing somewhat over that expected from the number of holes present in the liquid. In Flory's expression for the viscosities of polymers, above, there occurs a temperature-independent term involving the size of the molecule, namely, that

$$\eta = Ke^{aZ^{1/2}} \quad (10)$$

where Z is the weight-average number of atoms in the chains of the molecules making up a given polymer.

Some dependence of the viscosity on the total chain length is to be expected in any case: although we have seen that the flow of long chains is merely the resultant of the motions of segments of a definite size which jump about at a definite rate, independent of how many segments are joined together in a chain, it must be true that, due to the very fact that the segments are joined together by strong bonds, some coördination of movement between segments is necessary in order that the chain as a whole can progress. This requirement of the coördination of the helter-skelter motions of the segments causes more and more waste motion to occur as the chains get longer (more coördination being required for longer chains), so that the fluidity, which measures only the number of successful jumps, should decrease with increasing chain length. Furthermore, the fraction of successful jumps should not depend on the temperature, it being merely a function of the amount of coöperation which is required of the segments, while the total number of jumps per unit time is independent of the chain length and depends only on the size and nature of the segments, and on the temperature and pressure. That is

$$\text{fluidity} = \phi = 1/\eta = F(Z)G(\rho, T) \quad (11)$$

(11) L. Rotinjanz, *Z. physik. Chem.*, **62**, 609 (1908).

(12) See below for a discussion of this.

where F is the same function for all substances (if, as seems reasonable, though by no means certain, the same sort of coöperation between segments is required of all substances) and G depends on the nature of the polymer.

Flory's result, equation (10), says, of course, just this and gives to $F(Z)$ the form $e^{-aZ^{1/2}}$. The constant a , which is close to $1/4$ for the substances investigated by him, is very likely the same for all types of polymers. (This is the reason why we have used this same constant above in calculating the lengths of the chains in sulfur and in rubber.)

The fact that $F(Z)$ has the form of an exponential seems to us to be very significant, and can probably arise in only one way: it is well known that $e^{-x} \cong (1 - x/n)^n$ when n is a large number and $n \gg x$. Therefore, knowing the experimental result, we can say that the probability that a jump by a segment is successful in causing flow of the molecule as a whole is proportional to $(1 - 1/4Z^{1/2}/n)^n$, where n is some large number (perhaps the number of segments in the molecule). But this is merely the probability that n successive and independent events, each having the probability $(1 - Z^{1/2}/4n)$ of success, shall all be successful. $Z^{1/2}/4n$ is evidently the probability of failure.

Why the probability of failure should be equal to $Z^{1/2}/4n$ depends upon the criterion of an unsuccessful jump by a segment. The nature of this criterion has not yet been definitely established by the authors, but the following is probably not far from the truth.

A freely twisted hydrocarbon chain containing Z links can be shown¹³ to enclose on the average a volume of $3.4Z^{1/2}$ cubic Ångströms, while the chain itself occupies an actual volume of $20Z$ cubic Ångströms. Of the entire volume enclosed by the freely twisting molecule, only a volume $V_1 = 1/n(3.4Z^{1/2})$ can be said to be available to each segment (n being the number of segments). And in order for the movement of a segment to be successful, the segment must be located within some definite region of volume $V_2 = 20Z$ which the molecule will take up after moving under the action of the shear force. But the probability of failure, that is, the probability that the segment shall be in a space V_1 is

$$V_1/(V_1 + V_2) = V_1/V_2 = 3.4/20Z^{1/2}/n = 0.17Z^{1/2}$$

(V_1 being much less than V_2 , usually). The value of the coefficient of $Z^{1/2}$ is thus calculated to be

(13) W. Kuhn, *Kolloid Z.*, **76**, 258 (1936).

0.17 as against the value of 0.25 observed by Flory.

It is interesting to inquire what might happen to the viscosity when chains get very long. If, in what has been said above, n , the number of successive events required in order that an entire molecule can flow, is merely a very large but fixed number, then a value of Z can be reached such that n is no longer much greater than $Z^{1/2}/4$. Our replacement of $(1 - x/n)^n$ by e^{-x} will now no longer be valid and we shall obtain instead a relationship between the fluidity and some power of Z . This does not seem very likely, but until more is understood of the physical nature of the problem, it cannot be excluded.

A second possibility which might occur when chains become very long is that, in order for an observable shear rate to occur, such large forces are applied that chains are broken. The material may then act as if it were made up of shorter chains, *i. e.*, the apparent fluidity may increase.

The relationship of the above considerations to the flow of large molecules in solution would be of interest, especially at those concentrations at which collisions between chains are frequent. This will have to await the further development of the physical picture. So also will a consideration of which type of chain-length average (*i. e.*, weight average or number average) should be used in calculating Z in equation (10).

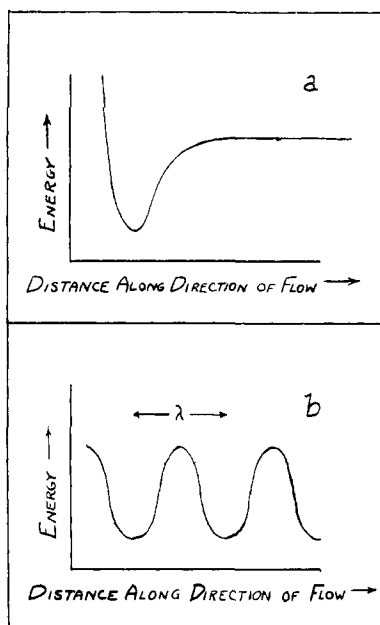
It is worth mentioning that we have investigated a further possible dependence of the viscosity on the chain length due to the fact that the polymers studied by Flory are not of uniform chain length. Then it is possible that the flow is simply that of large molecules embedded in small ones and will depend merely on the concentration of small molecules. This, however, cannot be thrown into an exponential form depending on chain length, so is excluded as a possible mechanism by the experimental results.

D. Non-Newtonian Flow.—Until now, we have been considering largely substances which can be treated by equation (2). Many substances made up of large molecules, however, show viscosities which vary with the magnitude of the applied shearing force, so require a different treatment. Since this subject of non-Newtonian flow is of great importance in the flow of many high molecular weight substances, it deserves some attention here.

(1) **Qualitative Discussion.**—Non-Newtonian flow may arise from two sources. It was shown in connection with equation (1) that if $f\lambda_2\lambda_3\lambda/2$ is

small in comparison with kT (*i. e.*, if the energy supplied in pushing the unit of flow into an empty hole is of the same order as kT), then the viscosity will depend on the magnitude of the shearing force. The second possible source of non-Newtonian flow involves a change in structure or flow mechanism as the rate of flow changes.

Equation (1) has been applied to the non-Newtonian flow of rubber by Smallwood, as we have seen above, and to the flow of synthetic resins by Kistler.¹⁴ It is urged that in applying equation (1) in this way, a fairly wide range of shearing forces and temperatures be used in order that the validity of the application of the equation to the particular case in hand can be established. If this is not done, questions can always be raised, whether the cause of non-Newtonian flow is not at least in part due to changing structure with different rates of flow. On the other hand, when the applicability of equation (1) has been definitely established, the magnitude of the "viscous volume," $\lambda_2\lambda_3\lambda$, may be determined, as well as ΔH^\ddagger and ΔS^\ddagger of activation. This can serve as a valuable check in estimating the size of the unit of flow, as we have already seen in the case of rubber.



Figs. 5a, b.

Changing structure with different rates of flow may occur in several ways. Molecules may "line

(14) S. S. Kistler, in publication. The authors wish to express their gratitude to Dr. Kistler for the opportunity of reading this manuscript.

up" to a greater and greater extent as the rate of shear is increased; that this actually occurs in many cases is shown by the fact that drawn threads and sheets of polymers often behave as anisotropic crystals, showing double refraction, X-ray fiber patterns, and different tensile strengths and other physical properties in different directions with respect to the flow direction. A study of the anisotropy produced by flow would provide valuable additional information concerning the mechanism of the flow, and is a highly desirable, as well as easily measured, piece of data to include in any investigation of the flow of large molecules.

When "lining up" of molecules occurs, equation (1) will still be applicable, but the constants occurring in it may vary with the rate and length of time of application of the shear force.

A second way in which changing structure may affect the type of flow occurs when bonds¹⁵ are broken between molecules or parts of molecules and the broken ends of the bonds do not immediately recombine with the loose ends of other bonds. The barrier preventing flow will then have the shape of Fig. 5a, rather than of Fig. 5b, on which the derivation of equation (1) is based. A fairly well defined yield point will occur, and the flow of the material for forces greater than those at the yield point will depend upon the relative rates of breaking and of recombination of the broken bonds (*i. e.*, upon the mean life of the activated state).

(a) If the rate of recombination of broken bonds is slow, as in those gels which require a long time to set, the flow above the yield point may be expected to be Newtonian since, once the bonds are broken, the only resistance to shear will be the ordinary viscosity of a liquid. Furthermore, once the yield point has been passed it may be possible to obtain Newtonian flow for shear forces below the yield point¹⁶ (see Fig. 6). This constitutes the most marked type of *thixotropy*, since such substances may be converted from solids or semi-

(15) The word "bond" is used here in its broadest sense, meaning any force tending to make atoms or molecules cohere.

(16) When flow takes place according to this mechanism an additional factor has to be guarded against by the experimentalist in order that he can be sure that he is actually measuring a viscosity. This is that as the yield point is reached, bonds will tend to break along one slip plane and the flow which takes place after the bonds are broken will be concentrated in a thin fluid layer between two undisturbed masses. The gradient of shear will then be very large, much larger than would be expected from the dimensions of the apparatus in which the measurements are being made. This results in an apparent viscosity which is much larger than the true viscosity of the fluid layer. Behavior of this type should be easily detectable by visual inspection of the material under shear.

solids into ordinary fluids merely by surpassing the yield point and it is probably illustrated by the iron oxide sols of Freundlich,¹⁷ some of which require several hours to gel.

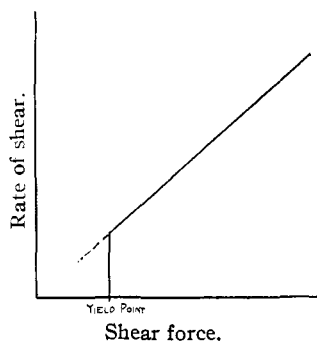


Fig. 6.

The striking behavior of rubber on mastication may also be interpreted on the picture of bonds breaking due to shear. It is a well known fact¹⁸ in the rubber industry that if rubber is masticated in the presence of oxygen, it gradually becomes softer, while in the absence of oxygen there is no softening. Furthermore, as the temperature is raised, the rate of softening in the presence of oxygen becomes slower, until a certain temperature is reached (about 240°), above which there is rapid softening. With ozone, on the other hand, there is rapid softening at all temperatures, with no minimum rate of softening at any temperature. This behavior is summarized by Fig. 7 (from reference (18)).

It would seem that the process of mastication involves the breaking of chemical bonds—perhaps of cross linkages, or perhaps of the chains themselves. The "catalytic" effect of oxygen has been ascribed to an increased reactivity of bonds (not necessarily double bonds) under stress, which makes them susceptible to some kind of bond-splitting reaction involving oxygen. A rather interesting and slightly different alternative explanation might involve the following: the process of mastication may result in the mechanical rupture of certain cross-linkages or chains; in the absence of oxygen, the loose ends (which are free radicals in the same sense that CH_3 and C_2H_5 are free radicals) will then merely recombine at the first opportunity, so that no reduction in the cross linking or of chain lengths results, and there is no softening.

(17) H. Freundlich, "Thixotropy," *Actualités Scientifiques et Industrielles*, 1935.

(18) See, for example, "Proc. Rubber Technology Conference," London, 1938, p. 388.

Oxygen, however, would react with the free radicals, making them incapable of recombining.

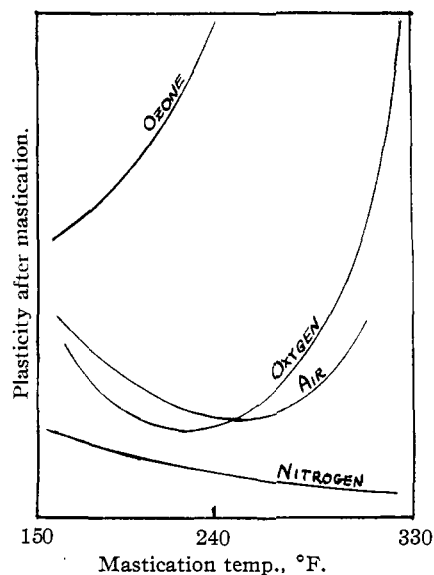
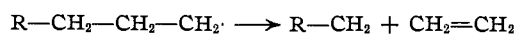
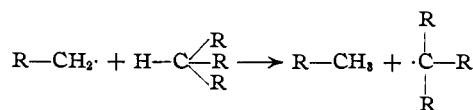


Fig. 7.

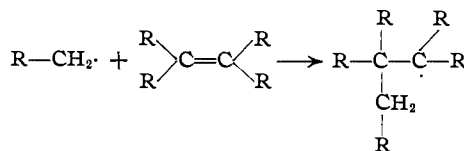
That such free radicals could exist for an appreciable time, even in such complex molecules as those making up rubber, is altogether possible, since it is difficult to see how a radical, once formed, could be destroyed by any intramolecular rearrangement. Such conceivable reactions as



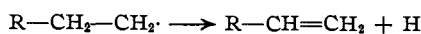
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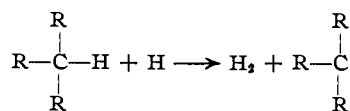
or



only result in a "migration" of a free bond from one atom to another, without destroying the possibility of re-forming the cross-linkages which prevent softening on mastication. Even such a reaction as



which destroys the radical, would be followed by



which forms a new radical.

The less rapid softening under mastication at higher temperatures is understandable if the molecules are able to flow more easily as a whole, so that large stresses are no longer accumulated in any of the bonds. At still higher temperatures the oxygen attacks the double bonds in the rubber molecules and breaks the chains without the aid of mechanical forces, so there is again softening. Ozone, on the other hand, is well known to be able to break double bonds even at low temperatures, so there is no minimum in the curve for ozone.

(b) If after breaking the bonds do re-form readily, an equilibrium will be set up between the breaking and re-forming of bonds, and a definite retarding force will operate. It should, however, be possible to shear rapidly enough that the bonds have no time to re-form, and at and above this rate of shear we will again have Newtonian flow as long as no turbulence sets in (Fig. 8). Curves of the type of Fig. 8 have indeed been observed experimentally.¹⁹

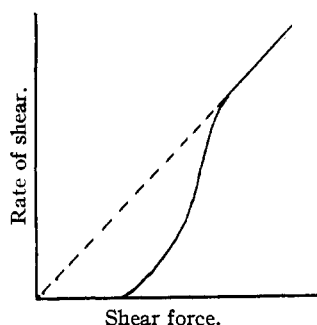


Fig. 8.

On the other hand, it is possible that increased rates of shear will, by increasing the number of collisions between broken ends of bonds, increase the rate of re-formation as well as the rate of breaking of bonds.²⁰ The phenomenon known as *rheopexy* (promotion of gelation by stirring) arises from this sort of behavior. In this case, we might reach a state at which there is a constant number of bonds, causing a constant "drag" independent of the rate of shear. This is equivalent to ordinary friction, except that there is usually superposed the Newtonian viscosity of some fluid which is also present, so that the situation illustrated by Fig. 9 is found. This type of relationship for plastic flow has been expounded chiefly by

(19) W. Ostwald and R. Auerbach, *Kolloid Z.*, **38**, 261 (1926).

(20) Cf. v. Schmoluchowski, in H. Freundlich's "Colloid and Capillary Chemistry," Methuen Co., New York, N. Y., 1926, p. 436.

Bingham.²¹ A good illustration of it is found in work of Lewis, Squires and Thomsen²² on suspensions of Bentonite in oil at different temperatures. Curves of the type shown in Fig. 9 were obtained, with the same yield point at all temperatures and the slopes of the lines above the yield point corresponded to the viscosities of the pure oils at the same temperatures.

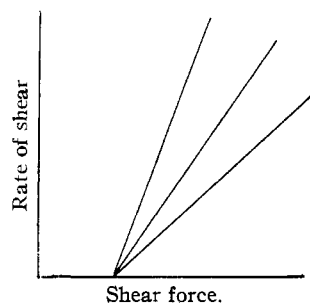


Fig. 9.

The phenomena of friction and lubrication appear to involve this type of equilibrium between rate of breaking and re-formation of bonds.

(2) **Quantitative Treatment of Non-Newtonian Flow.**²³—Consider the model illustrated in Fig. 10. Two plates, separated by a distance λ_1 , are tied together by m_0 elastic bands. A fluid is also present between the plates. A shear force F is applied to the plates, stretching out the elastic bands so that the plates are unable to pass each other freely unless the bands break. As the force F approaches the tensile strength of the bands, the bands begin to break, one by one. If the bands do not re-form after they break, the plates will move past each other more and more rapidly as more

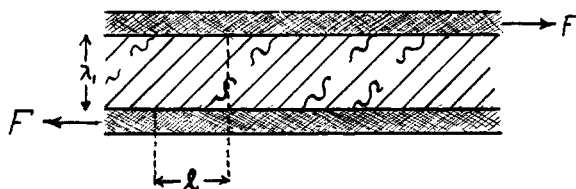


Fig. 10.

and more bands break. When no more bands remain, the plates will move past one another at a rate determined by the viscosity of the fluid between the plates. This is the situation discussed in (a), above, the elastic bands being replaced by

(21) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922, p. 215.

(22) W. K. Lewis, L. Squires and W. I. Thomsen, *Am. Inst. Mining Metall. Engrs.*, **118**, 71 (1936).

(23) Cf. C. F. Goodeve, *Trans. Faraday Soc.*, **35**, 342 (1939); E. Orowan, *Z. Physik*, **89**, 605ff. (1934).

bonds of some sort, and the plates by neighboring layers of moving molecules. And in the mastication of rubber, oxygen merely acts to prevent the recombination of the bands when they have broken. In what follows the contribution to F due to the viscosity of the fluid between the plates is neglected, since it is readily allowed for.

When the bands do recombine, however, there are always some of them present to hold back the two plates, and the relationship between force and rate of shear becomes more complicated. We shall now indicate how this relationship can be treated from a knowledge of the properties of the molecules making up the system.

Suppose that under a given shear force F , bands are re-forming as rapidly as they are breaking, so that at any given time there are m bands joining the two plates. Of these, only a fraction, αm are stretched out and exert any force on the plates, since some of the bands have been re-formed too recently for the plates to have moved far enough for them to be stretched again appreciably. (Obviously, a band formed by the combination of two loose ends will be relaxed.) The velocity with which the plates pass one another will be given by the product of the number of bands which break per second, $(dm/dt)_{\text{breaking}}$ and the distance, λ , which the layers move as a result of the release of strain when one band breaks

$$\Delta v = \lambda(dm/dt)_{\text{breaking}} = \lambda_1 F/\eta \quad (12)$$

λ is determined as follows: the length, l , of the projection of a band on the direction of flow (see Fig. 10) is determined by the average force acting on each stretched chain, which is given by $f = F/\alpha m$. Thus

$$l = l(F/\alpha m) = l(f) \quad (13)$$

Then

$$\lambda = -(\partial l/\partial m)_F = -dl/df(\partial f/\partial m)_F = +f/m dl/df \quad (14)$$

$(dm/dt)_{\text{breaking}}$ is determined in turn by applying the theory of absolute rates of reaction to the calculation of the rate of breaking a bond which is being stretched by a force, f . Let the potential function for the bond be given by a Morse function (see Fig. 11a)

$$V(r) = D(1 - e^{-a(r-r_0)})^2 \quad (15)$$

where r is the length of the bond, r_0 is the equilibrium separation of the atoms, D is the dissociation energy, and a is given by $\sqrt{k/2D}$, k being the force constant of the bond in the neighborhood

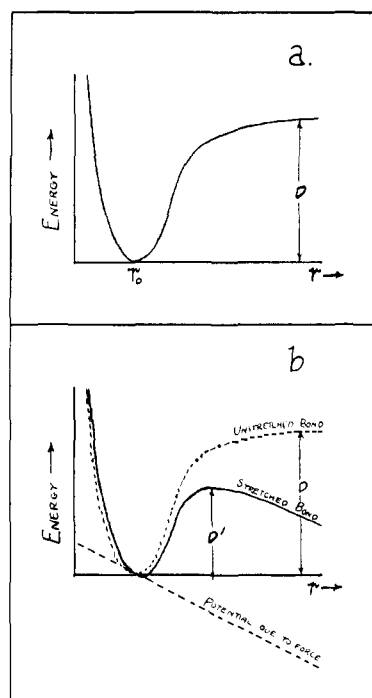


Fig. 11.

of the equilibrium separation.²⁴ In order to break a bond of strength D when the bond is not undergoing any vibrations, an energy D must be supplied. If, however, the bond is under tension due to a constant force f pulling on either end, the activation energy required to break the bond is diminished (see Fig. 11b) from D to D' . A simple calculation²⁵ will show that for any force f , the fraction of the original activation energy, D , required to break the bond is given by

$$D'/D = x \log \left(\frac{1-x-\sqrt{1-2x}}{x} \right) + \sqrt{1-2x} \quad (16)$$

where $X = F/Da$. This function is plotted in Fig. 12.

Knowing the activation energy, the rate of breaking bonds is given by the expression for a unimolecular reaction

$$(dm/dt)_{\text{breaking}} = (\alpha m k T/h) e^{\Delta S^\ddagger/R} e^{-D'/RT} \quad (17)$$

If we knew the number of bonds m which are unbroken and the fraction α of them which are under stress, we could use (17) and (14) in (12) to find the relationship between shear force and the rate of shear, which is what we are seeking. In order to find the value of the shear force, we must know

(24) Other types of functions than Morse functions may, of course be used to describe the potential energy of a bond; cf. Orowan, ref. (22).

(25) See, e. g., J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).

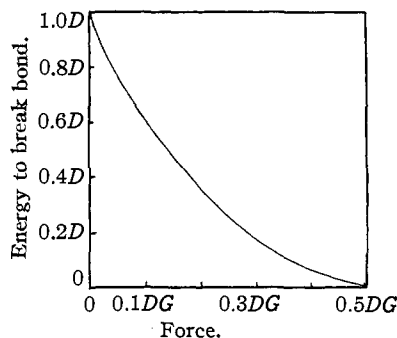


Fig. 12.

the expression for the rate of recombination of broken bonds. Most simply, this would follow a bimolecular rate law

$$(dm/dt)_{\text{breaking}} = k'(m_0 - m)^2 \quad (18)$$

where k' is a rate constant not usually depending on anything but the temperature for a given system. If the rate depends on the rate of shear, due to an increased number of collisions at higher rates of shear, this must be accounted for in (18).²⁰ All that now remains to be done is to set $(dm/dt)_{\text{breaking}} = (dm/dt)_{\text{forming}}$, which will be true at equilibrium, and solve for m in terms of F , α , and perhaps Δv . α is probably usually close to unity, so that we have a means of eliminating m from equation (12), and there remains an expression involving only F and Δv , the shearing force and rate of shear, which can then be evaluated in terms of one another and of the quantities m_0 , dl/df , D , a , ΔS^\ddagger , and k' . The latter, except perhaps for k' , can be estimated fairly readily from the known structure and physical properties of the material. k' may be determined from the rheopectic and thixotropic behavior of some substances, and it may be estimated theoretically for others, but, in general, this will cause the most trouble in the application of the present method, or any other method for that matter.

Although the actual evaluation of the relationship of F and Δv by means of equations (12), (14), (17) and (18) will in general prove very cumbersome, this is merely a consequence of the complexity of the entire problem. Further development of the equations must await a later date, but some information concerning the behavior of the yield point under various conditions is readily obtainable from equation (17). The yield point can be defined as the point at which flow begins to be noticeable experimentally. Since flow can only occur when bonds break at a certain rate, $(dm/$

$dt)_{\text{breaking}}$ must have a definite value at the yield point. Furthermore, at the yield point, $m = m_0$, so we may write (17) as

$$(dm/dt)_{\text{breaking}}^{\text{yield point}} = m_0 A e^{-D/R TG(F/m_0 D a)} = \text{constant} \quad (19)$$

where DG is the function plotted in Fig. 12. It is readily seen from this equation that as long as m_0 is constant with temperature, the yield force should not depend on the temperature very markedly, since both F and T occur in the exponential. On the other hand, if m_0 varies with the temperature, as, for instance, in a region of shifting equilibria, m_0 would depend upon the temperature exponentially. But m_0 itself occurs in the exponent along with the force, so that the force at the yield point will now change very rapidly with the temperature. Actually, both types of behavior of the yield point are observed but, as would be expected, it is much more common for the yield point to be rather insensitive to the temperature.

E. Relaxation Times of Polymers.—The conclusion that long chains flow in segments is of some interest in connection with the dielectric behavior of polymers, so that brief notice is appropriate here. It seems likely that very much the same treatment can be given to the heats and entropies of activation in the process of a dipole's rotating to follow an alternating field as has been given above for the determination of the size of the units of flow in macromolecules. The result would probably be similar here, namely, that the rotating element is made up of only relatively few atoms, but there is little reason to expect that any coöperation between segments is required here, so there should be no dependence of relaxation times for dielectric behavior on the size of the molecule as a whole as long as the molecule contains more than a few atoms.

Another type of hysteresis behavior which could be studied profitably by the present method is the rate of release of strain in stretched rubber. According to the so-called statistical theory of rubber,²⁶ the elasticity of rubber is due to the tendency of the long chains of which rubber is made to assume random spatial orientations. This being granted, then the rate of relaxation of rubber on releasing stress should give a measure of the rate at which the chains are able to assume random orientations. The temperature dependence

(26) H. Mark, *Chem. Rev.*, **28**, 121 (1939).

of this rate should tell something about the size of the units through which the readjustment takes place.

F. Rates of Polymerization and Condensation as a Function of Molecular Size.—It is of some interest to the kineticist to know something of the rate at which reactants diffuse through a reaction mixture. If this rate of diffusion is very slow, the usual statistical mechanical or kinetic theory rate expressions may not be applicable since equilibrium conditions may not be maintained throughout the reaction mixture. It has been argued that the very high viscosities of some polymers may give rise to such a state of affairs. From what we know of the viscous behavior of polymers, however, it would appear that as long as no more than one large molecule is involved in a reaction taking place in a molten polymer, there should be no influence of the viscosity on the rate of the reaction, since, just as the individual segments of a long chain jump about at a rate independent of the total chain length, so small molecules should be able to jump about at a constant and rather rapid rate, which is independent of the over-all lengths of surrounding chains and hence of the viscosity of the mixture. Even if reacting groups located on two different macromolecules take place in a given reaction, it seems likely that there is sufficient articulation among segments as to allow freedom of movement over a considerable region, so that diffusion processes may not even be important here in influencing the rates of reactions involving large molecules.

The notion of a long chain's being made up of small segments, which with regard to most phenomena act as more or less independent molecules, seems to us to argue rather strongly in favor of

Flory's²⁷ contention that the over-all length of a chain has no influence on the reactivity of a group occurring in that chain, and that "steric factors" depending on chain length, such as were used by Dostal,²⁸ are unwarranted.

We wish to take this opportunity to express our gratitude to Dr. W. O. Baker for a helpful discussion.

Summary

The statistical mechanical rate equation is utilized to ascertain the mechanism of the flow of large molecules. It is shown that as hydrocarbon chains increase in length, they do not flow as a single unit, but tend to flow as segments which average roughly twenty atoms in length. This movement by segments of twenty to forty atoms is generally characteristic of large molecules. The viscosities of longer hydrocarbons are larger than would be expected from the simple concept of holes as recently applied to the problem of viscosity. This effect is also shown in the recently reported proportionability of viscosity to $e^{aZ^{1/2}}$, where Z is the length of the chain for long chain molecules. The latter relationship is shown to arise from the requirement that the random motion of segments of a large molecule must be coordinated in order that the molecule as a whole can move in the direction of flow. The treatment of non-Newtonian and plastic flow in terms of the rate equation is outlined and the results discussed qualitatively. The significance of the findings to the problems of dielectric relaxation and of rate processes involving large molecules is indicated.

PRINCETON, NEW JERSEY

RECEIVED JULY 30, 1940

(27) P. J. Flory, *THIS JOURNAL*, **61**, 3334 (1939).

(28) H. Dostal, *Monaish.*, **67**, 63 (1936).