The corresponding values calculated by Kolthoff at 18° are

$$K_4' = 5.35 \times 10^{-11}$$
$$K_5' = 7.38 \times 10^{-23}$$

An interesting fact with respect to mercuric oxide is that the position of minimum solubility appears to be that in water solution (see Fig. 4 which includes data given by Garrett and Hirschler[1]). This is to be expected since Kolthoff has indicated that the pH of water solutions of mercuric oxide at 18° is approximately 7.2. It is also to be observed that the value[1] of K_6 for the reaction

$$H_2HgO_2 \rightleftharpoons H^+ + HHgO_2^- \qquad (6)$$
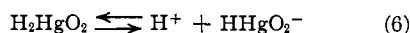
is

$$K_6 = 1.4 \times 10^{-15}$$

and the ion product is 3.4×10^{-19}; while the value of K_4' for the reaction

$$Hg(OH)_2 = Hg(OH)^+ + OH^- \qquad (4)$$
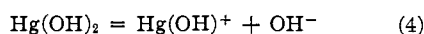
is

$$K' = 7.1 \times 10^{-12}$$

and the ion product is 1.7×10^{-15}. The similar magnitude of K_4' and K_6 and of the ion products of these two reactions is further evidence of a nearly neutral hydroxide and therefore one which would be expected to give its minimum solubility at approximately pH = 7. In fact both the m_{H^+} and the m_{OH^-} contributed by the mercuric hydroxide are less than the concentration of these ions produced by water; however, the $m_{OH^-} > m_{H^+}$. This indicates the minimum solubility might be expected to be slightly on the basic side. These very low values of m_{H^+} and m_{OH^-} contributed by the dissociation of mercuric hydroxide

serve to explain the fact that the conductivity of aqueous solutions of mercuric oxide is about that of the solvent itself.

The character of the solid phase was established by analysis for the nitrate ion and for the mercury content, respectively. This was particularly necessary at the high acid concentration where one might expect basic salt formation. The solid phase was separated from the mother liquor by filtration; it was washed quickly in the filter crucible with two small portions of water to remove adsorbed nitric acid and analyzed with standard potassium iodide solution. All samples except one analyzed to mercuric oxide and gave negative nitrate tests.

Summary

The solubility of mercuric oxide has been determined in nitric acid solutions ranging from 0.00005 to 0.16 molal. The constants for the dissociation of mercuric hydroxide have been evaluated from these data. The values of these constants are in good agreement with the fact that mercuric hydroxide solutions have a very low conductivity and give a pH value of approximately 7. They are also in agreement with similar constants obtained from e. m. f. measurements (Kolthoff). The data indicate that the minimum solubility is in water solutions, that mercuric hydroxide dissociates in a stepwise manner, and that the H$^+$ and OH$^-$ contributed by mercuric hydroxide in water solution are less than those contributed by the solvent.

The Viscosity Function. II.[1] Viscosity and Constitution

BY ERNEST P. IRANY

The graphical method of analyzing viscosity data by means of functional viscosity scales has revealed a great number of general regularities in the dependency of viscosity on temperature, volume (ideal dilution) and pressure. One may reasonably expect some relation between viscosity and chemical constitution to be derivable by the same or analogous means.

However, before this can be attempted it is

important to realize the difficulties arising from the uncertainty which still surrounds the concepts to be dealt with. We are not yet able to define the liquid state or to recognize the real meaning of constitution within it. Molecules, as described by their chemical formula, exist in gases but not in the crystal lattices of solid bodies; all that can be said about liquids is that their molecules must be in some intermediate condition: neither as mobile and independent as in gases nor as fixed and diffused as in solids. Precisely what

the physical units of liquid constitution are—single molecules, more or less permanent and more or less well-defined groups of molecules, or even some kind of organized structure—remains a matter of speculation.

Association, Intermolecular Forces.—When considering the existence in liquids of units composed of several molecules or molecular structures of some kind, strong binding forces must be assumed. The problem of viscosity now divides itself, for, should viscosity be correlated with the intensity of these intermolecular forces or with the association of molecular volumes which they may bring about? The forces as well as the volumes partake of constitution, whatever it be.

This distinction is very decisive for the approach to the problem of constitutional viscosity. Most modern authorities still prefer to connect viscosity with variously defined additive volumes or weights which are held to be a property of certain atoms or atomic groups. Often the disregard of the intermolecular forces is very explicitly stated.[2] However, as shown in the following, volume or weight association of the physical units does not as such provide a valid interpretation of constitutive viscosity.

Association Factors.—The paraffin hydrocarbons are known to be "non-polar" or "non-associated"—in their case the controversial aspects of constitution are absent. They are available in a very long and unbroken series of homologs and, as a matter of course, they are always chosen as the first objects of study in the verification of a new rule of constitutional additivity. It is mostly very easy to show regular increments in no matter what terms, but agreement usually fails as soon as the new formula is applied to other types of liquids which, presumably, are more "polar" or "associated." If the latter view is adhered to, agreement with facts may be enforced by specifying "association factors" which are supposed to denote a bodily enlargement of the molecular unit. These factors disagree widely, depending on their source; whether they possess real significance or whether they merely reflect the inadequacy of the original premises can only be decided by independent evidence.

Such proof can be found in the viscosity–temperature functions of polar as well as non-polar liquids of various types. If represented in the

(2) Bingham, "Fluidity and Plasticity," 1922, p. 148, etc.; McLeod, *Trans. Faraday Soc.*, **21**, 151 (1925); Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

functional ϕ scale, all appear as perfectly straight lines. This accord in linearity can only mean that all liquids except some, such as the lower alcohols and fatty acids, are either non-associated or that their state of association is entirely independent of temperature. The suggested association factors are fractional numbers, indicating the liquids to be mixtures of several species of multiple molecular size; that such equilibria should be unaffected by large temperature changes is, however, barely conceivable. Hence: *The association factors as deduced from empirical rules of constitutionally additive viscosity are not real; most liquids are not associated and the rules thus amended are wrong.*

If, then, association of molecules does not suffice to explain liquid constitution in its relation to viscosity, the whole basis must be altered. The intermolecular forces must be included in the concept of constitution, without implying that they actually cause associative combinations. These forces, the resultants of equilibria within the molecules, cannot be computed—least of all as mere sums of some atomic constants. However, where variable association occurs, it can be recognized by the graphical method of functional scales; it reveals itself in deviations from linearity.

The Equation of the Liquid State.—The explicit mathematical or graphical statement of nature and physical behavior of a liquid would be its equation of state. Without argument on its exact form, it may be said that this basic function correlates the three variables of condition—volume, pressure and temperature; it must contain general constants and also various specific material constants—parameters in which the nature of the substance, in other words, its constitutive elements, are expressed. Among the latter the regularities must be detected which govern viscosity.

The three viscosity functions (that of volume (dilution), that of temperature and that of pressure) are, in combination, a complete expression of the equation of state in parameter form. The functional scales employed in the graphical method of generalization are common to all normal liquids and, hence, embody the general constants of the equation of state; the individually descriptive constants must appear as intercepts or gradients of the straight lines which record and distinguish the function of each substance. The

question now arises as to how many of these constitutive elements of viscosity are necessary and sufficient.

Number of Material Factors.—One given viscosity measurement determines one point in each of the three functional diagrams; in order to determine a line, another point must be given in each figure—which brings the total to four (Fig. 1). However, two of the functional scales—that of ideal mixture (volume) and that of temperature—are identical; in other words, volume and temperature are of the same relevance with respect to constitution. (The temperature function may be considered a special case of dilution, *i. e.*, with a solvent of no viscosity or a void.) Accordingly, the number of independent constitutional factors reduces from four to three.
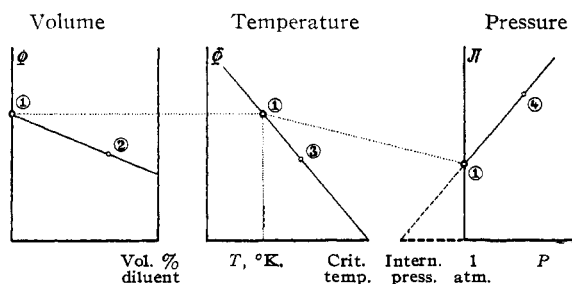

Fig. 1.—Constitutive parameters of the viscosity functions.

The viscosity of liquids is not appreciably affected by pressures of several atmospheres. It is entirely correct to assume that, ordinarily, viscosity measurements are compared under strictly "corresponding" conditions with regard to pressure—at the external pressure nil. This dispenses with another material constant, leaving only two. Further simplification is not possible. Hence: *No rule of constitutive viscosity can be generally valid unless it postulates two independent parameters of different computation.*

To recognize the necessity of two constitutional constants is one step, but to define them in such a way that they become additive in terms of atomic values is another, far more difficult one, which cannot be attempted here. This problem is most complex with the most simple chemical compounds because among them every structural difference is large enough to obscure all physical relationship. Additive increments can only be expected in certain series of homologous substances in which the intermolecular forces are either negligible or constant for all members:

for example, (a) homologous series of non-polar substances, (b) polymer-homologous series of substances which are composed of a large and variable number of identical polar groupings.

The former are represented by the normal paraffin hydrocarbons, the latter by various polyvinyl derivatives. In both cases one of the two constitutive parameters becomes a serial constant; the other is, therefore, uniquely descriptive of the individual member and additive in any terms of structure, such as molecular volume, molecular weight, number of constituent groupings, degree of polymerization—all of which become synonymous. It must be kept in mind, however, that this final simplification applies only within series of the above description; the absence of this limitation is the common error which invalidates the numerous single-parameter rules of additive viscosity and the supplementary association factors.

Paraffin Hydrocarbons.—If the viscosities are plotted in ϕ scale against reduced absolute temperatures, T/Θ,[1] (Fig. 9) the lines of the members of this series coincide almost completely. Hence, $\phi = CT/\Theta$, where C is a serial constant, and Θ, the critical temperature, appears as the constitutive parameter. The problem resolves to that of the critical temperature and its additivity; reversely, the critical temperature of a hydrocarbon can be computed from a single viscosity measurement. That the whole series—though not absolutely "non-polar"—is distinguished by very weak intermolecular forces which are the same for each member, can be proved in the functional viscosity–pressure diagram (II scale); the extrapolated internal pressures have a constant value of about 1200 kg./cm.[2] (Fig. 11[1]).

Polymer Homologs.—Since most of these substances are high-molecular colloids, the distinction by critical temperatures is meaningless; the constitutive parameters must be defined
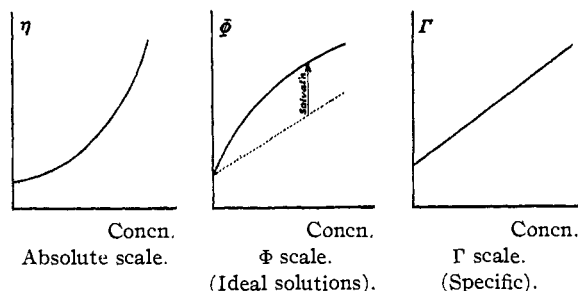

Fig. 2.—Polyvinyl acetate solution.

through the viscosity–concentration function of solutions. The series of polyvinyl acetates may serve as an example.
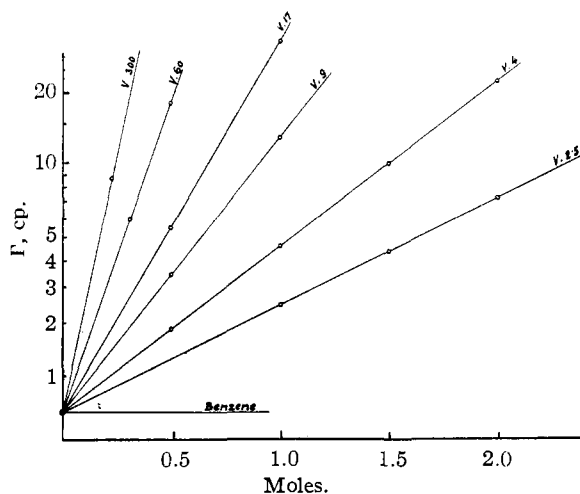

Fig. 3.—Polyvinyl acetates, benzene solutions.

If the viscosities of polyvinyl acetate solutions are plotted in ϕ scale against concentration, no straight lines appear, but curves whose trend indicates strong associative or solvating effects between solute and solvents of various description (Fig. 2). Since all polyvinyl acetates consist of regularly repeated identical groupings, the disposition of their intermolecular forces must be the same and characteristic of the whole series. The polar effects which cause the deviations from linearity in the ϕ scale diagram can, therefore, be expressed as a single serial constant which may be incorporated into the viscosity scale. This can be done by the same graphical method as that applied in the construction of the ϕ scale itself (Fig. 2[1]), except that in the present case not an "ideal" mixture but, specifically, a polyvinyl acetate solution is used as a standard. The resulting viscosity scale Γ embodies the serial polarity as well as the concentration effects of *all*

polyvinyl acetates in a given solvent, *e. g.*, benzene (Fig. 3). The lines shown in the diagram are perfectly straight and differ only in their gradients; the latter represent the individual constitutive parameter—the degree of polymerization.[3]

Analogous viscosity scales can be constructed for other solvents, such as ethyl acetate, butyl acetate, pyridine, dioxane, chloroform, tetrachloroethane, acetic acid. In each case accurate linearity for polyvinyl acetates of every degree of polymerization is obtained. These scales are, by precept, specific for each solvent. However, it is most significant that, actually, a majority of them have been found one and the same. It must be concluded that all solvents of this group induce the same state of solvation, that they respond to a certain normal polarity of the solute, revealing a characteristic regularity in the associative tendencies of polyvinyl acetates.

If the gradients of the lines in the various diagrams represent, as concluded, the respective degrees of polymerization, they should appear
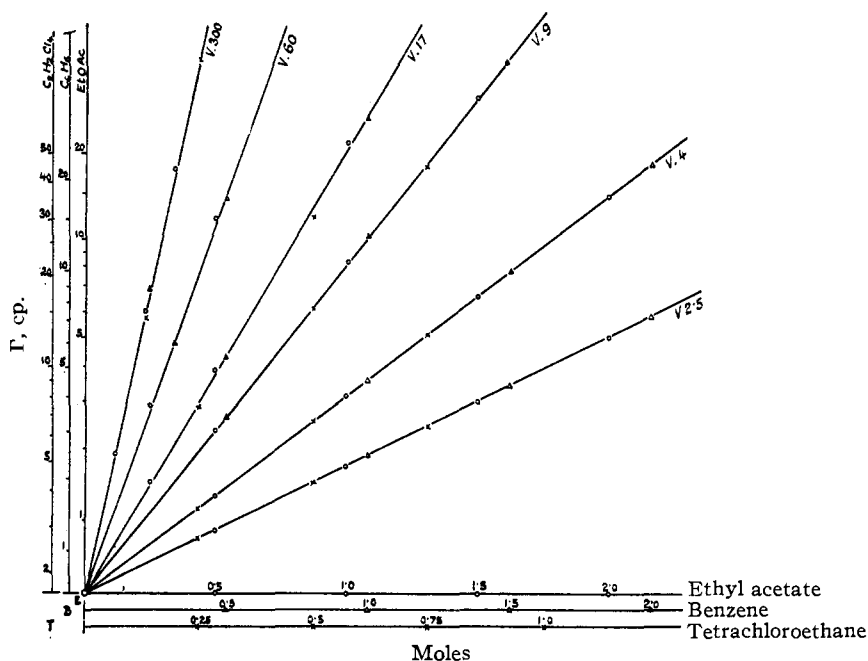

Fig. 4.—Polyvinyl acetates (Gelva).

in proportions fixed by the nature of the samples. That this is true with the greatest precision is

(3) Polyvinyl acetates ("Gelva," manufactured by Shawinigan Chemicals, Ltd.) are mixtures of high and low polymers over a wide range. The mean degree of polymerization is indicated in the figures by "V ..." which is the viscosity of the sample in one-molar (86 g./1.) benzene solution at 20°.

shown in Fig. 4, where the viscosities of one specimen ("V.4") in three solvents, *viz.*, ethyl acetate, benzene and tetrachloroethane, are plotted on the same straight line. The origin of this line represents the viscosities of the respective
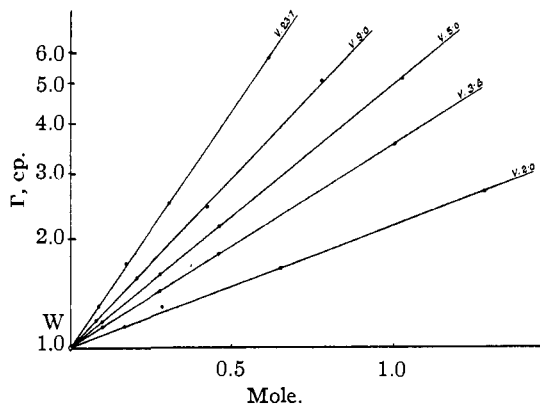

Fig. 5.—Polyvinyl alcohols in water.

pure solvents, and the scales are adjusted accordingly. As a result, the lines of the three solutions of each sample coincide; the complete Γ diagrams of ethyl acetate, benzene and tetrachloroethane solutions of polyvinyl acetates register exactly when superimposed. Hence, the gradients are independent of the solvent but descriptive of the solute.

That the same regularities exist in the solutions of all true polymer homologs can be shown by many other examples, such as the water-soluble polyvinyl alcohols (Fig. 5),[4] the polyisobutylenes (Fig. 6),[5] various cellulose derivatives (Fig. 7). All these substances give linear concentration functions in their own characteristic viscosity scales which compensate for association and solvation effects common to all members. In some series these effects are absent; they, therefore, appear linear in the ideal ϕ scale. Examples of these are indene resins, toluene sulfonamide resins, colophony, chlorinated diphenyl resins, etc. (Fig. 8). In order to illustrate the deviations of the specific Γ scales from ideality, an ideal mixture is plotted in the diagrams which appears strongly curved in all cases except Fig. 8.

(4) "Solvar" (Shawinigan Chemicals, Ltd.).
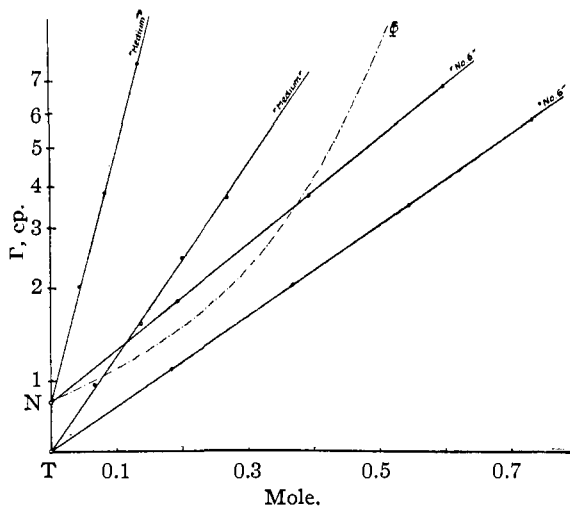(5) "Vistanex" (Advance Solvents & Chemical Corp.).

Fig. 6.—Poly-butylenes ("Vistanex") in V. M. naphtha (N) and in toluene (T).

Molecular Weights.—That the gradients of the lines in the Γ diagrams appear in the proportions of the molecular weights of the solutes can be made clear by analogy to Staudinger's "viscosity law."[6] The latter is based upon a formula by Einstein[7] which expresses the viscous resist-
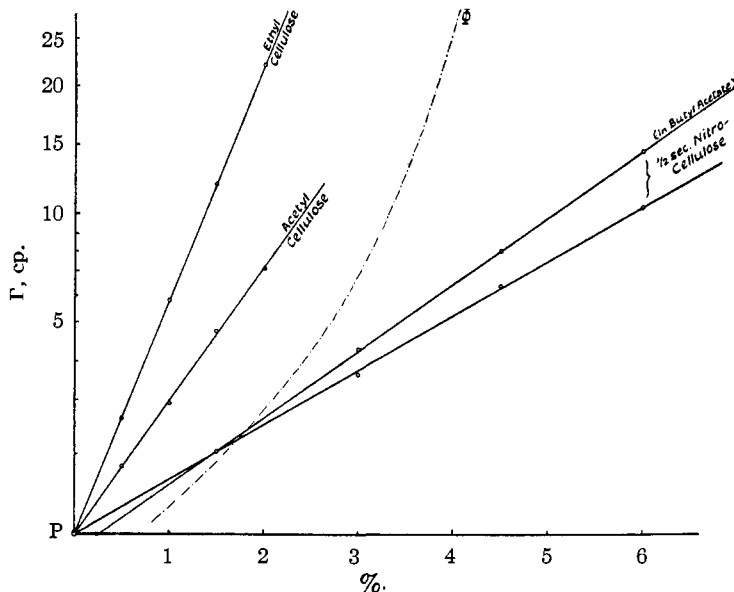

Fig. 7.—Cellulose derivatives in pyridine.

ance in an ideal case—that of spherical, rigid and non-polar particles dispersed in a viscous liquid—but without assumption of mutual attractions. Because of the disregard of the latter, the formula is not applicable to real solutions, but under

(6) Staudinger, "Die hochmolekularen Verbindungen," Verlag J. Springer, Berlin, 1932.
(7) Einstein, *Ann. Physik*, **19**, 289 (1906).

the limitation of minimum concentration, Staudinger transformed it into

$$\eta_{sp} = \lim_{c=0} \frac{\eta - \eta_0}{\eta_0} = K_m M c \qquad \lim_{c=0} \frac{\eta - \eta_0}{c} = (\eta_0 K_m) M$$

where η_{sp} is termed "specific viscosity," K_m is a constant valid for a given polymer-homologous series in a given solvent, M the molecular weight and c the concentration.

In a diagram where absolute viscosity is plotted against concentration, the term $(\eta - \eta_0)/c$ appears as the gradient of the curve in the vicinity of the origin (Fig. 9). The same figure, drawn in Γ

Staudinger's law.   Gamma function.

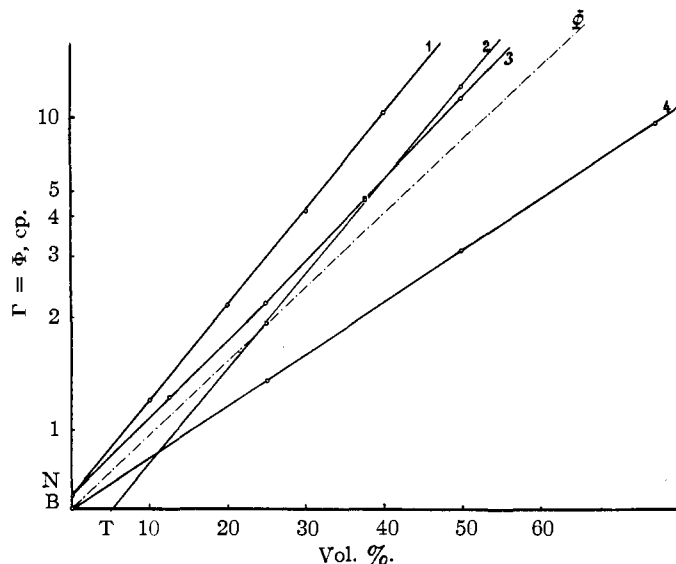Fig. 9.—Molecular weight of polymer homologs.

Fig. 8.—No solvation: 1, indene resin (Nevindene) in butyl acetate; 2, toluene sulfonamide resin (Santolite MHP) in toluene; 3, rosin in butyl acetate; 4, chlorinated diphenyl (Aroclor) in V. M. naphtha.

scale, represents the curve as a straight line of constant gradient; there is no need to limit the rule to low concentrations. Accepting the reasoning that led from Einstein's formula to that of Staudinger as substantially correct, the substitution of Γ for η would, according to definition, compensate for the effects of intermolecular forces at *any* concentration

$$\Gamma_{sp} = \frac{\Gamma - \Gamma_0}{\Gamma_0} = K_m M c$$

Γ_{sp}/c, now to be termed "specific viscosity function," is the gradient of the straight line in the Γ diagram. In other words, if a line is drawn
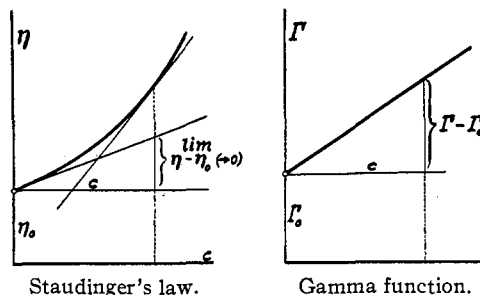
parallel to the viscosity axis, the intercepts on it are in proportion of the molecular weights of the solutes, or, more correctly, their individual constitutive parameters which may be expressed equally well in terms of molecular weights, volumes, chain lengths, number of constituent units, etc.

Summary

Graphical analysis of viscosity data shows that most pure chemical compounds are unassociated in the liquid state. The association factors which, while derived from empirical rules of constitutionally additive viscosity, are necessary to uphold their validity, have no meaning.

It can be proved that the general viscosity function contains not less than two independent constitutive parameters. It therefore appears impossible to specify single atomic constants supposed to be additive in terms of viscosity.

The best approach to the problem is not through the study of the most simple chemical compounds, but that of truly polymer-homologous series of high-molecular substances. In the latter case, one parameter, expressing the polar character common to all members of the series, is constant and the second parameter becomes constitutionally additive. This has been proved by graphical evidence on various such series.

The method of analysis is an extension of the principle of the functional viscosity scales reported in a preceding paper to which reference is made.

SHAWINIGAN FALLS   RECEIVED MARCH 6, 1939
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