

Determination of Molecular Weights from the Activation Energy for Viscous Flow of Liquids

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reported equation⁷ for the intrinsic viscosity of chain molecules, it is thus found:

$$\bar{h}^2 = 16 \times 10^{-16} \text{ cm}^2 \text{ (chloroform solution, } \nu \gg 1; \text{ from viscosity measurements). (6)}$$

The close agreement of the calculated value (5) and of the actual value (6) is much better than might be expected. Probably this is to some extent accidental; in general, it will have to be assumed that the values of constants a and b and thus the \bar{h}^2 values will be somewhat dependent upon the solvent used.

¹ K. S. Pitzer, J. Chem. Phys. **8**, 711 (1940).

² H. Kuhn, Habilitationsschrift, Basel (June 1946). The same Eq. (2) has been obtained recently also by W. J. Taylor, J. Chem. Phys. **15**, 412 (1947). An equation that represents the special case of (2) for free rotation has been given by H. Eyring, Phys. Rev. **39**, 746 (1932), and an equation valid for nearly free rotation has been reported by C. Sadron, J. Chem. Phys. **43**, 12 (1946). P. Debye got in an unpublished work recently an equation, representing another special case of (2), namely, the case that only part of the rotational angle ϕ_k is allowed and that there is a constant probability distribution in the allowed range. (Reported after H. Benoit, Report of a lecture at the High Polymer Conference, Strasbourg, November, 1946.)

³ W. Kuhn, Koll. Zeits. **68**, 2 (1934), see also reference 5.

⁴ H. Kuhn and O. Künzle, to be published.

⁵ W. Kuhn and H. Kuhn, Helv. Phys. Acta **26**, 1293 (1943); *ibid.* **28**, 1533 (1945); *ibid.* **29**, 71 (1946).
⁶ W. O. Baker, C. S. Fuller, and J. H. Heiss, J. Am. Chem. Soc. **63**, 2142, 3316 (1941). In that paper are reported viscosity measurements of ω -hydroxy-undecanoic acid polymers. We assume that there is no considerable difference in \bar{h}^2 of that polymer and of a hydrocarbon with the same number of chain members, i.e., it is assumed that the

disturbing influence of the few $\text{—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{—}$ groups in the chain, each of

which making up for two CH_2 members, can be neglected.

⁷ H. Kuhn and W. Kuhn, in preparation; previously reported by W. Kuhn and H. Kuhn, Helv. Phys. Acta **30**, 1233 (1947).

Determination of Molecular Weights from the Activation Energy for Viscous Flow of Liquids

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October 3, 1947

THE following equation has been recently proposed by the writer:¹

$$\eta = Ze^{\gamma(M/D-d)^{\frac{1}{2}}} \cdot N^{\frac{1}{2}}/RT, \quad (1)$$

where η = the viscosity, γ = the surface tension, M = the molecular weight, D and d are the orthobaric densities of the liquid and vapor, respectively, N = the Avogadro number, Z = the "frequency factor," R = the gas constant, and T = the absolute temperature. However, for theoretical reasons which will be incorporated in a forthcoming paper, Eq. (1) has now been slightly modified as

$$\eta = Ze^{\gamma(M/D-d)^{\frac{1}{2}}} \cdot N^{\frac{1}{2}}/(\cos 30^\circ)^{\frac{1}{2}}/RT, \quad (2)$$

or,

$$\ln \eta = \ln Z + \gamma \left(\frac{M}{D-d} \right)^{\frac{1}{2}} \cdot \frac{N^{\frac{1}{2}}}{(\cos 30^\circ)^{\frac{1}{2}}/RT}, \quad (3)$$

or,

$$\log_{10} \eta = \log_{10} Z + \frac{0.4343 \cdot N^{\frac{1}{2}}}{(\cos 30^\circ)^{\frac{1}{2}} \cdot R} \cdot M^{\frac{1}{2}} \cdot \frac{\gamma/(D-d)^{\frac{1}{2}}}{T}. \quad (4)$$

One of the ways in which (4) can be tested is to utilize it for the determination of molecular weights as shown below.

If T_1 and T_2 are sufficiently close to each other, Z may be assumed to be a constant, and below the boiling point d becomes negligible in comparison with D . On the basis of these assumptions, and writing the subscripts 1 and 2 for the respective values at T_1 and T_2 , it follows from (4) that

$$\log_{10} \eta_1 - \log_{10} \eta_2 = \frac{0.4343 N^{\frac{1}{2}}}{(\cos 30^\circ)^{\frac{1}{2}} \cdot R} \cdot M^{\frac{1}{2}} \left\{ \frac{\gamma_1/D_1^{\frac{1}{2}}}{T_1} - \frac{\gamma_2/D_2^{\frac{1}{2}}}{T_2} \right\}. \quad (5)$$

Rearrangement of (5) gives

$$M = 3.176 \left\{ \frac{\log_{10} \eta_1/\eta_2}{(\gamma_1/D_1^{\frac{1}{2}} \cdot T_1) - (\gamma_2/D_2^{\frac{1}{2}} \cdot T_2)} \right\}^2 \quad (6)$$

expressing R and γ in the same units. Hence, we can see that the molecular weight can be determined from the experimental values of η , γ , and D at two temperatures.

TABLE I.

Substance	Melt- ing point °C	Tem- pera- ture °C	Vis- cosity 10 ³ η	Sur- face ten- sion γ vap.	Dens- ity D	Mole. wt. M calc. from (6)	% Devia- tion
Benzene	5.5	0.0 20.0	9.00 6.47	31.70 29.02	0.9000 0.8790	80.54	+3.1
Ethylene dibromide	10.01	10.0 20.0	(2.034) [†] (1.718) [†]	40.05 38.75	(2.2014) 2.1805	179.8	-4.3

[†] 10³ η .

The necessary data given in Table I for purposes of illustration have been taken from the *International Critical Tables*, and the values given in parentheses have been calculated from the formulae given in the *I.C.T.*

Considering the possibility that some uncertain factors might have been incorporated in the utilization of (6), the agreement between the theoretical and the observed value of the molecular weight may be deemed to be satisfactory. The uncertainties involved may be the unknown reliability of viscosity data; moreover, a temperature difference of 10° or 20° may be too much for assuming the value of Z to be a constant. It has been found that the molecular weight calculated from (6) at higher temperatures decreases gradually with increasing temperature, and it is observed to be a characteristic of other liquids also, such as chloroform, ether, etc. It is to be concluded, therefore, that the method is reliable only near the melting point of a substance. This behavior is not surprising in view of the derivation of (2), which is based on the assumption that a liquid has a structure resembling that of a solid, and this would be true in the neighborhood of the melting point only.² At higher temperatures, thermal agitations may cause a considerable amount of disturbance of this structure.

The main purpose of this paper has been to point out that we have here a new method by which we can determine the molecular weight of a substance in its pure state. Most of the hitherto existing methods of molecular weight determination are applicable to solutions or vapors which may not give the correct picture of the pure liquid state. For instance, vaporization may decompose a substance or

alter the molecular complexity, and in the dissolved state, combination between the solute and the solvent may take place. The method proposed in the present paper is being extensively tested by the writer.

¹ M. S. Telang, *J. Chem. Phys.* **15**, 525 (1947).

² The theoretical basis of this derivation will be the subject of a future paper by the writer.

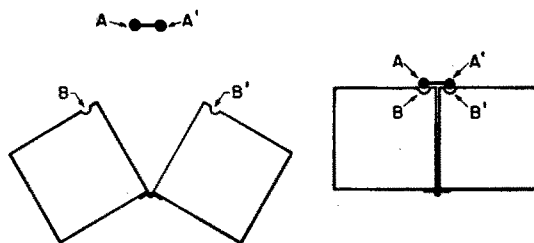


FIG. 1.

A Possible Contributing Mechanism of Catalysis

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October 15, 1947

IT seems remarkable that organic catalysts, and most inorganic ones, have a large mass, often much larger than that of their substrate. For example, catalase is about 10,000 times heavier than H_2O_2 . It may, therefore, be worth while to consider types of mechanism in which the mass of the catalyst could play a role.

It is generally assumed that the effect of a catalyst is to establish some course for the reaction to follow which does not involve as high an energy of activation as the uncatalyzed reaction. A catalytic effect would also be afforded, however, by establishing a course in which the reaction is accompanied by a large increase in the entropy of the catalyst.

Calling S the substrate and S' the product of the reaction catalyzed by C , the reaction might involve the following steps:

(1) $S + C \rightarrow SC$ accompanied by a moderate release of energy and a large loss of entropy.

(2) $SC \rightarrow S'C$ requiring a large activation energy E but accompanied by a regain of the entropy lost in (1).

(3) $S'C \rightarrow S' + C$ accompanied by a moderate uptake of energy.

If, for example, the loss of entropy Δs in (1) were equal to $E/2T$, the rates of reaction of (1) and (2) would be both moderately slow, being proportional, respectively, to $\exp(-\Delta s/R) = \exp(-E/2RT)$ and to $\exp[(\Delta s/R) - (E/RT)] = \exp(-E/2RT)$, but far higher than the rate of the uncatalyzed reaction.

Consider now the possible influence of the mass of a catalyst on this type of reaction, for example, in a case where $S = A - A'$, $S' = A + A'$. Step (1) of the reaction might be further resolved into:

(1a) $A - A' + C \rightarrow CA - A'$ accompanied by a moderate release of energy and no loss of entropy.

(1b) $CA - A' \rightarrow CA + A'$ accompanied by a further moderate release of energy and a large loss of entropy. As a concrete model, S might be a particle suspended in water and consisting of two blocks hinged together carrying specific receptor spots B and B' (for A and A') at the positions indicated on the sketch. Step (1a) may then occur according to the usual picture, step (1b) when the blocks happen to come in the right configuration; the absorption of A' onto B' then locks the blocks together, preventing their free rotation. This entails a loss of entropy of the

order of $R \log(IkT/\hbar^2)^{1/2}$, where I is the rotational moment of inertia of the hinged blocks and R , k , T , and \hbar have their usual meaning. The quantity in parentheses is of the order of magnitude of 100 for diatomic molecules and may be taken as 10^7 for an enzyme of molecular weight between 10^4 and 10^5 . The resulting entropy change affects the free energy by about 5000 calories, an amount which is not large but yet is significant. From an atomistic standpoint it may be said that Brownian fluctuations of the pressure of water molecules on the large faces of the blocks tend to tear the bond between A and A' .

In general, a catalyst of this type might be described as a particle so constructed that: (a) a very low zero-point energy corresponds to some of its internal degrees of freedom (this can happen only if the mass of the particle is large), and (b) those degrees of freedom can be nearly frozen in a particular configuration by specific absorption of a substrate molecule, so that their zero-point energy is thereby raised very much. For comparison it is recalled that the entropy increase in the reversible denaturation of proteins is equivalent to more than 50,000 calories.

Dr. J. E. Mayer, to whom I am also indebted for other suggestions, pointed out that step (2) in the reaction above would have a high temperature coefficient corresponding to the full activation energy E while its rate is determined by the lower free energy change $E - T\Delta s$. In fact, the temperature coefficient of enzymatic reactions is rather low.

This discrepancy and the result of the numerical calculation above make it unlikely that the mechanism suggested here is the main factor of catalysis. It may, however, be one among several concurrent factors of comparable importance.

The Dependence of Quenching Efficiency on Temperature

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October 13, 1947

A SMALL cross section for the process in which electronically excited atoms are quenched by other molecules may be theoretically associated with a small temperature coefficient if the non-adiabatic step or entropy of activation is the principal factor restricting the occurrence