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A Contribution to the Theory of Viscous Flow Reactions for Chain-Like Molecular Substances

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Ewell and Eyring investigated a relation for the coefficient of internal friction as a reciprocal reaction rate employing a large number of data. In this paper these investigations are extended to new data involving homologous series of higher esters. The variation of the activation heats of the flow process with temperature, molecular weight, and constitution, is considered and an attempt made to correlate it to the molecular constitution. There are indications that the above-mentioned ideas contain implicitly through Stefan's theorem a relation between surface tension and viscosity.

THE quantum mechanical transition-state method,¹ so successful for reaction kinetics, was applied by Eyring and Ewell² to the theory of transport phenomena in liquids. The flow process is considered as a chemical reaction, in which every molecule passes from one equilibrium position over a potential barrier in an adjacent one. The slower the reaction rate, the smaller the diffusion constant and the larger the viscosity.

In a large number of cases it could be shown that the activation energy of the "flow reaction" amounts to a more or less constant fraction $1/n$ of the internal evaporation energy. We shall later on revert to this point. Especially interesting are those cases like water, in which changes of n occur with the temperature. In this way, it is possible, under certain circumstances, to obtain information about changes of the internal state of the fluid, e.g. dissociation or association, respectively, and curling up of chain molecules.

These questions have a great scientific and technical importance for the recognition of the structure of pure liquids as well as of solutions. Last, but not least, is the investigation of fluids with long chain molecules, also important as a transition for the understanding of high molecular weight substances. These often cannot be

kept in the melted nor in the dissolved state in consequence of the large molecular attraction.

It seemed desirable to examine the data of Albert and Eirich³ on esters in the above-outlined direction. Moreover it is possible in this way, to furnish a semi-empirical relation between two quantities characteristic for the intermolecular forces, *viz.* the surface tension and the viscosity.

The reliability of the evaporation energies must be examined critically before employing them for the determination of the ratios evaporation energy/activation energy since they were determined semi-empirically rather than experimentally. The extrapolation of the Stefan factors in the $E_{\text{vap}} - \sigma$ relation in respect to molecular weights is burdened with an uncertainty even for the nonylic acid and naturally is greater for the esters of nonylenic and oleic acid. But the comparison of the results with the experimentally determined behavior of the paraffins and the consistency with the values for the evaporation heats resulting from the additivity rule, respectively, seem to eliminate the principal objections. That is also valid for the use of the factors for nonylic acid in the case of the esters of nonylenic acid. As the molecular surface tensions are equal, the boiling points and the evaporation energies of saturated and unsaturated compounds are similar, larger changes of the factors are not to be expected. The assumption of constant values for the several esters of the homologous series is in principle wrong, but

¹ A detailed report of this theory is found in Trans. Faraday Soc. **34** (1938). Compare also H. Mark and R. Simha, "Atomphys. Grundlagen d. chem. Katalyse," *Handbuch der chemische Katalyse* (J. Springer, Berlin, in press).

² H. Eyring, J. Chem. Phys. **4**, 283 (1936); R. H. Ewell and H. Eyring, *ibid.* **5**, 726 (1937), in the following designated with I, and II., R. H. Ewell, J. App. Phys. **9**, 252 (1938).

³ O. Albert and F. Eirich, Zeits. f. physik. Chemie **A183**, 9 (1938).

the magnitude of the error is not significant. It will become evident at the end, that even greater uncertainties do not much influence the determination of the n values, and, avoiding all the uncertainties by employing molecular surface energies instead of evaporation heats, we do not change the nature of the conclusions.

In order to determine the activation energy E_{vis} of the flow process, we plot, as usual, $\ln k$, and in this case $\ln \eta$ against $1/T$. Fig. 1 shows these curves for the first three esters of the formic and acetic acid ($F_{1, 2, 3}$, $A_{1, 2, 3}$), for the propionic methylester and for allylacetate (P_1 , \bar{A}_3), for the first three esters of nonylic and nonylenic acid ($N_{1, 2, 3}$, $\bar{N}_{1, 2, 3}$), and finally for the first five esters of the oleic acid series (O_{1-5}). The data for the low molecular esters were taken from the Landolt-Börnstein tables, in order both to put our conclusions on a broader base and to have a transition from the substances treated in II to ours.

For the F , A and P esters and those of the nonylenic acid, one obtains with remarkable accuracy straight lines. For N_{1-3} and O_{1-5} the functions are represented by curves smoothly bent against the $1/T$ axis, which, however, have a practically constant slope in the region of about 300–400K. Similar curves were obtained by Eyring and Ewell for the paraffins higher than C_{10} . Unfortunately the given material provides too little data in order to draw the curves in an entirely definite way and to determine the differential quotients graphically. Therefore the difference quotient was first calculated in the approximately linear region. Then, for greater accuracy, representation of the temperature dependence of η by an analytical expression was tried, thus:

$$\eta = AT^s e^{Q/RT}. \quad (1)$$

Here A , s and Q are established as temperature independent parameters⁴ and are computed from the three most distant points. Values of s of 3.5 to 5.5 mean a temperature dependence of the frequency number and therefore of the entropy of activation of the flow reaction. In calcu-

⁴ One has generally to assume a temperature dependence of Q and also of A ; compare, for instance, E. N. da C. Andrade, Phil. Mag. 17, 698 (1934) and A. G. Ward, Trans. Faraday Soc. 33, 88 (1936). Considering the small curvature, this was not necessary.

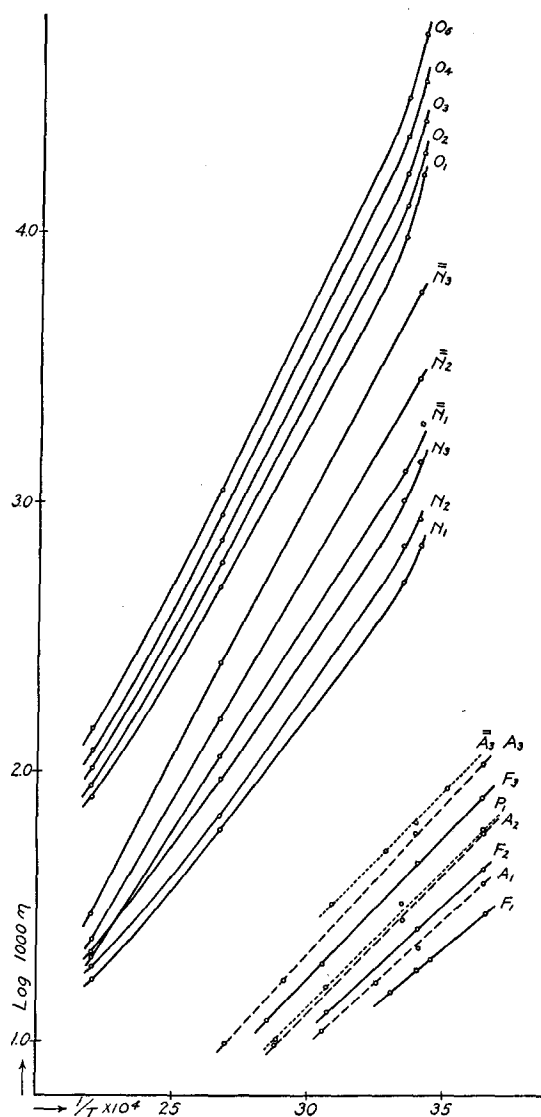


FIG. 1.

lating with the aid of the so-found values the fourth and further points of the curve, one finds discrepancies of no more than maximally 0.1 between measured (or graphically interpolated) and computed points.

On principle it is further possible to apply the statistical methods for the calculation of the entropy factor, also to reactions of the kind considered in this paper, as did Eyring in I. However, several factors enter which are difficult to determine. Therefore here, as in II, an empirically given entropy of activation was assumed.

The activation heat of a monomolecular

transformation is defined by⁵

$$E = -R \frac{d \ln k}{d(1/T)}. \quad (2)$$

For the flow reaction we obtain by consideration of (1)

$$E_{\text{vis}} = R \frac{d \ln \eta}{d(1/T)} = Q - sRT. \quad (2a)$$

In the corresponding columns of the Tables I to IV the values of the calculated activation heats and directly determined activation heats, respectively, are found. Besides in the Tables II and IV the slopes of the straight regions are also indicated. The next column shows the ratios of evaporation and activation energies. As these ratios are mostly temperature dependent, the n values, given in the last column, were constructed at different corresponding temperatures, indicated in brackets; namely for a better comparison in the case of low boiling substances at

TABLE I.

SUBST.	°K	E_{vap}	$\frac{E_{\text{vis}}}{R} = \frac{\Delta \ln \eta}{\Delta \left(\frac{1}{T}\right)}$	$\frac{E_{\text{vap}}}{E_{\text{vis}}}$	n
Methyl	290	6.48	1.66 _s	3.90	4 ($\frac{4}{3}$)
	303	6.26		3.76	3.5 (b.p.)
	313	6.06		3.64	—
Ethyl	273	7.37	1.87	3.94	4 ($\frac{4}{3}$)
	323	6.61		3.54	3.5 (b.p.)
Propyl	273	8.74	2.08 _s	4.19	4 ($\frac{4}{3}$)
	353	6.97		3.34	3.5 (b.p.)
	363	6.75		3.24	—
Methyl	293	7.40	1.84	4.02	4 ($\frac{4}{3}$)
	333	6.54		3.55	3.5 (b.p.)
Ethyl	273	8.32	2.01	4.14	4 ($\frac{4}{3}$)
	353	6.86		3.42	3.5 (b.p.)
	373	6.53		3.25	—
Propyl	293	8.92	2.20	4.05	4 ($\frac{4}{3}$)
	373	7.41		3.37	3.5 (b.p.)
	383	7.22		3.28	—
Methylpropionate	313	7.68	1.98	3.88	4 ($\frac{4}{3}$)
	343	7.17		3.61	—
	353	6.97		3.52	3.5 (b.p.)

⁵ R. C. Tolman, *Statistical Mechanics* (Chemical Catalogue Company, 1927), pp. 259–69; V. K. La Mer, *J. Chem. Phys.* **1**, 289 (1933).

TABLE II.

NONYLIC ACID ESTER	°K	$-T \cdot \frac{d}{dT}(\sigma v_m)^{\frac{1}{3}}$	$\frac{E^*_{\text{vap}}}{F \cdot u_g}$	$R \frac{\Delta \ln \eta}{\Delta \left(\frac{1}{T}\right)}$	$\frac{E_{\text{vis}}}{Q - sRT}$	$\frac{E_{\text{vap}}}{E_{\text{vis}}}$	n
Methyl	298	789	13.2 ₂	2.70	3.1 ₀	4.2 ₆	4 ($\frac{4}{3}$)
	373	990	11.2 ₅		2.5 ₆	4.4 ₀	4.5 ($\frac{4}{3}$)
	453	1200	9.2 ₃		1.9 ₉	4.6 ₃	—
Ethyl	298	822	13.8 ₀	2.96	3.3 ₁	4.1 ₇	4 ($\frac{4}{3}$)
	373	1030	11.7 ₄		2.6 ₅	4.4 ₃	4.5 ($\frac{4}{3}$)
	453	1250	9.6 ₃		2.0 ₁	4.7 ₈	—
Propyl	298	860	14.4 ₈	3.10	3.3 ₉	4.2 ₇	4 ($\frac{4}{3}$)
	373	1077	12.3 ₀		2.9 ₀	4.2 ₄	4 ($\frac{4}{3}$)
	453	1309	10.1 ₀		2.3 ₈	4.2 ₄	—

* $u_g = 2.02 \cdot [\sigma v_m^{\frac{1}{3}} - Td/dT(\sigma v_m^{\frac{1}{3}})]$; F (according to Albert and Eirich) for 298° = 3.72, 373° = 3.15, 453° = 2.60.

the boiling point and $\frac{4}{3}$ of the boiling temperature, for higher boiling substances at $\frac{4}{3}$ and for further comparison with the still higher boiling oleic acid esters also at $\frac{3}{2}$ b.p. In determining the n we always rounded off to the next integer or half integer.

The data in the tables can be summarized as follows:

Table I. (a) The n vary from 3.5 at the b.p. to 4.0 at $\frac{4}{3}$ b.p. The ratios and therefore the n decrease with increasing temperature. Rounding off in the same way as Eyring did, one obtains in agreement with his results $n=4.0$. (b) The ratios at the b.p. decrease with increasing molecular weight.

Table II. (a) At $\frac{3}{2}$ b.p. results $n=4$, at $\frac{4}{3}$ b.p. $n=4.5$. At the boiling point we have therefore to expect $n=5$. (b) The ratios remain practically constant with increasing molecular weight. (c) With increasing temperature they increase a little.

Table III. (a) Surprisingly the ratios and n values at $\frac{3}{2}$ b.p. are 4, but decrease to 3.5 at $\frac{4}{3}$ b.p. and tend towards a limit 3. (b) They decrease also with increasing molecular weight.

Table IV. All the esters of oleic acid have $n=5$ at $\frac{3}{2}$ b.p. As the quotients remain almost constant against changes of the temperature, one cannot expect alterations of this value. Also with the molecular weight definite changes do not occur.

One has to try to relate the n values for the four groups to probable properties of the molecules or of the corresponding liquids. Ewell and Eyring find for molecules, which do not deviate much from the spherical form, a fraction $1/n = \frac{1}{3}$.

TABLE III.

NONYLENIC ACID ESTER	°K	$-T \cdot \frac{d}{dT}(\sigma v_m^{\frac{1}{2}})$	$E_{\text{vap}}^* = F \cdot u_{\sigma}$	$E_{\text{vis}} = \frac{R \Delta \ln \eta}{\Delta \left(\frac{1}{T}\right)}$	$\frac{E_{\text{vap}}}{E_{\text{vis}}}$	n
Methyl	298	762	13.2 ₂	3.09	4.2 ₈	4 ($\frac{3}{2}$)
	373	955	11.2 ₅		3.6 ₄	3.5 ($\frac{4}{3}$)
	453	1160	9.2 ₅		2.9 ₉	—
Ethyl	298	804	13.9 ₂	3.42	4.0 ₇	4 ($\frac{3}{2}$)
	373	1006	11.8 ₅		3.4 ₇	3.5 ($\frac{4}{3}$)
	453	1222	9.7 ₅		2.8 ₅	—
Propyl	298	823	14.5 ₀	3.73	3.8 ₉	4 ($\frac{3}{2}$)
	373	1030	12.3 ₀		3.3 ₀	3.5 ($\frac{4}{3}$)
	453	1251	10.0 ₅		2.6 ₉	—

* See Table II.

Higher values originate from special bonds. Reductions are always found in the case of elongated molecules, possibly through preference of a flow direction. One has, therefore, to expect $n=3$ for symmetrical molecules, $n<3$ in the case of associations, while $n\sim 4$ for elongated ones, perhaps through compensation of two influences: fixation by orientation against the greater facility for flow in the direction of the longest axis. Ewell and Eyring consider it remarkable that even from so elongated molecules as paraffins with 18C atoms only $n=4$ values result. They assume that above all the curled molecules are activated for the flow process.

Before applying these ideas to our results we have to mention a point overlooked by Ewell and Eyring, namely, the decreasing of n with rising temperature for normal substances as seen, for instance, from Table I. We believe this is caused by a certain quality of the model. The n decrease because the heats of evaporation show a temperature dependence in accord with Kirchhoff's theorem, while E_{vis} as activation heat remains, generally and for our material in many cases, constant over a large temperature range. These changes of n are likely to have no special importance for the flow process, but are only a consequence of the decrease of E_{vap} .

For N_{1-3} and \bar{N}_{1-3} one obtains again $n=4$; for O_{1-5} , however, one obtains 4.5–5. In the first place it seems easy to explain this increase by assuming that the oleic acid esters are less curled up than the paraffins of the same chain length, which is plausible as consequence of the O—COgroup and particularly of the double bond.

TABLE IV.

OLEIC ACID ESTER	°K	$-T \cdot \frac{d}{dT}(\sigma v_m^{\frac{1}{2}})$	$E_{\text{vap}}^* = F \cdot u_{\sigma}$	$R \frac{\Delta \ln \eta}{\Delta \left(\frac{1}{T}\right)}$	$E_{\text{vis}} = \frac{E_{\text{vap}}}{Q - sRT}$	$\frac{E_{\text{vap}}}{E_{\text{vis}}}$	n
Methyl	298	966	20.6 ₀	3.67	4.4 ₅	4.6 ₂	5 ($\frac{3}{2}$)
	373	1208	17.6 ₅		3.6 ₄	4.8 ₅	
	453	1469	14.8 ₅		2.7 ₇	5.3 ₆	
Ethyl	298	987	21.1 ₅	3.88	4.4 ₁	4.8 ₀	5 ($\frac{3}{2}$)
	373	1234	18.0 ₅		3.7 ₄	4.8 ₂	
	453	1500	15.2 ₂		3.0 ₃	5.0 ₂	
Propyl	298	1010	21.8 ₀	3.96	4.4 ₃	4.9 ₂	5 ($\frac{3}{2}$)
	373	1263	18.5 ₃		3.8 ₁	4.8 ₇	
	453	1536	15.5 ₅		3.1 ₅	4.9 ₄	
Butyl	298	1058	22.5 ₅	4.12	4.6 ₈	4.8 ₂	5 ($\frac{3}{2}$)
	373	1322	19.2 ₇		3.9 ₇	4.8 ₅	
	453	1610	16.1 ₆		3.2 ₂	5.0 ₂	

* See Table II; F (according to Albert and Eirich) for 298° = 4.10, 373° = 3.50, 453° = 2.95.

This explanation may be right in this or some other cases. Nevertheless it becomes more difficult the more data are considered.

It is, for instance, striking that the nonylenic acid esters behave differently from those of nonylic and oleic acid and show the same temperature dependence of E_{vis} and n as the low esters. Presumably this is connected with another remarkable fact, namely, that the double bond can raise quantities related to the cohesion forces as density or surface tension, while others as evaporation energies remain practically constant and the melting points decrease. Considering our present knowledge of the structure of long chain molecules, it is not impossible that the shape stretched by the double bond, allows for a closer packing in the fluid state in contradistinction to the behavior of low molecular compounds, where it lowers the density. Nevertheless, it is more difficult for these molecules to arrange in a lattice.

These considerations can be correlated to the fact, that the constant values of A and Q are presumably not real, but are rather a result of a contrary variation of the two quantities. The longer a molecule is, the more essential must be its shape, as described by the inner-molecular statistics for the entropy factor. Two mechanisms are conceivable. Following the first the distribution of more flattened and curled up molecules is changed in favor of the latter ones with rising temperature. Besides the equilibrium

between inter- and intramolecular forces will turn out in such a way that a deviation from the most probable shape in vacuum will occur. In order to utilize better the intermolecular fields, the molecules will take shapes which are statistically (referred to the vacuum) less probable, but potentially more favorably orientated.

The data in this paper are not as extensive as those of Eyring and Ewell, but on the other hand they comprise a larger temperature range and treat in more detail one special class of substances.

We obtain the following results:

(1) E_{vis} is $\frac{1}{3}$ to $\frac{1}{4}$ of E_{vap} , whereupon viscous flow can be understood as one dimensional evaporation process, sometimes facilitated through orientation.

(2) $\ln \eta$ as logarithm of a reciprocal reaction rate varies linearly with $1/T$. E_{vis} , therefore, is constant and is not a temperature independent fraction of E_{vap} .

(3) Under the influence of the temperature dependence of the shape of long chain molecules, E_{vis} as well as the entropy factor can be temperature dependent or finally the compensating action of both can be disturbed. The graph $\ln \eta$ vs. $1/T$ is no more a straight line and n can change with T in any way.

One gets the following explanation for the behavior of our substances. For the shorter esters as normal liquids the points (1) and (2) are valid. For the longer nonylic acid esters and the paraffins, one must also consider point (3). It is plausible that the n values in this case increase with the temperature and that therefore E_{vis} decreases more quickly than E_{vap} , in respect to the small association always present in such long molecular substances. In this way, the contradiction that the n values of the curled-up molecules increase with temperature instead of decreasing, which was not observed by Eyring, since his considerations were restricted to a small temperature range, no longer exists. It may be noticed that the value $n=4$ discussed in II for paraffins applies only for the chosen temperature which in no way corresponds to the temperature at which the other factors were determined.

Following these ideas, one can easily understand the behavior of the unsaturated esters. In the case of the nonylenic acid esters the double

bond divides the molecules in two parts which are so short that the bending is not an important factor. Therefore these substances behave in respect to the absolute values as well as the changes in temperature of the n very similarly to the shorter esters. The slight differences are presumably connected with the fact that the first substances are saturated and that the determination of corresponding states for saturated and unsaturated fluid substances is doubtful in taking into account the irregular melting points.

The similarity in the behavior of the oleic acid and the nonylic acid esters is attributable to the fact that the parts of the former which are formed by the double bond are approximately just as long as the entire molecules of the latter and therefore possess sufficient internal mobility. The large, almost linear range between approximately 300–400K, which is caused by a similar, but less complete compensation than that of the normal substances, is delimited by two curvatures. One has to assume two different effects, namely, at room temperature the existence of a small association⁶ and at higher temperatures the effects of temperature upon the shape.

The activation energies show a rather regular increase with the molecular weight. The ratios E_{vap}/E_{vis} , on the contrary, decrease for \overline{N}_{1-3} and the lower esters, and remain almost constant for the other substances. In the latter case the evaporation heats increase in the same way as the activation heats, but in the former case for the shorter and more rigid molecules, they increase more slowly. These as well as the former considerations show that although a far-going analogy between evaporation and flow reaction may exist, characteristic differences in details occur. We mention this self-evident fact in the hope that if we pursue these differences, they will furnish further information about the mechanisms occurring in fluids.

Finally, formula (1) gives a relation between the surface tension of a fluid and its viscosity. For the internal evaporation heat is connected with the surface energy by means of the relation

$$E_{vap} = F[\sigma v_m^{\frac{2}{3}} - T(d/dT)(\sigma v_m^{\frac{2}{3}})],$$

⁶ E. E. Walker, Phil. Mag. **47**, 513 (1924).

where the Stefan-factor F is temperature dependent and has to be determined empirically in every special case. Nevertheless, it does not vary much for the most normal substances and for temperatures between 20 and 150°C, namely, from about 2.5 to 3.5. Therefore, F can be cancelled approximately against n in the expression $E_{vis} = E_{vap}/n$ or replaced by values between 0.7 and 1. (For our esters 0.84–0.93 for room temperature.) It means that the activation energy in the straight part of the curves is

nearly equal to the molecular surface energy and therefore;

$$\eta = A \exp \{ [\sigma v_m^{\frac{2}{3}} - T(d/dT)(\sigma v_m^{\frac{2}{3}})] / RT \}. \quad (3)$$

By this fact our conclusions are also freed from the assumptions made in determining the evaporation energies and could in a similar way be discussed in terms of surface energies in the place of evaporation heats.

We wish to thank Professor Victor K. La Mer for many helpful discussions.

Intensities of Electronic Transitions in Molecular Spectra

III. Organic Molecules with Double Bonds. Conjugated Dienes

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(Received December 9, 1938)

This paper is the first of a series on the application of intensity calculations to the spectra and related properties of organic compounds containing conjugated or resonating double bonds. It is concluded that in most cases the characteristic strong absorption of such compounds (giving color if the number of conjugated double bonds is large enough) is due to an $N \rightarrow V$ transition (homopolar normal state \rightarrow ionic excited state) similar to those already identified in paper II for I_2 , O_2 , C_2H_4 , and other molecules.

The present paper is devoted primarily to conjugated dienes. Unconjugated dienes and polyenes are treated incidentally, and it is shown theoretically that their ultraviolet spectra should be similar to those of alkenes (C_2H_4 and derivatives). There should be no strong absorption peak above $\lambda 2000$, and the intensity per double bond should be about the same as in alkenes. These conclusions are in agreement with the rather scanty experimental data (examples, diallyl, rubber).

Detailed calculations are made on 1, 3-butadiene by the molecular orbital method, assuming all the atoms to be in one plane. The results are applicable also to other conjugated dienes. Four $N \rightarrow V$ transitions must occur for the *unsaturation* electrons, i.e., those electrons which make the second or weaker bond in double bonds. This group of four transitions corresponds to the one $N \rightarrow V$ transition in alkenes; according to the calculations, the total absorption intensity per double bond is considerably increased by conjugation, especially if the molecules are in the *trans*-form. Conjugation causes the frequencies of the four transitions to scatter toward both longer and shorter wavelengths as compared with alkenes; as Hückel's work

implicitly shows. Although the calculated frequencies of the four transitions are independent of the shape of the molecule (within the range of reasonable assumptions), their intensities are very different for the *cis*- and *trans*-forms, and are also very sensitive to the bond angles. There is a marked tendency for the intensity to concentrate in the longer wave-length at the expense of the shorter wave-length $N \rightarrow V$ transitions, especially for the *trans*-form. In the latter, nearly all the intensity is concentrated in the longest wave-length of the four $N \rightarrow V$ transitions. This gives an essential clue to the explanation of the spectra of molecules containing conjugated polyene chains, e.g., carotene and related pigments, as will be shown in VI of this series.

Comparison of the theoretical predictions with available data on the ultraviolet spectra of dienes shows in general good agreement if we suppose that butadiene and its derivatives exist in the *trans*-form, except that perhaps its centrally-substituted derivatives (e.g., isoprene) exist partly in the *cis*-form. This conclusion is in line with other evidence. The available data are, however, somewhat conflicting, and systematic new measurements on the ultraviolet spectra of dienes and polyenes would be extremely valuable. The cyclic dienes, which are necessarily *cis*, show much weaker absorption in their longest wave-length $N \rightarrow V$ absorption region than do the open-chain dienes, just as predicted; the cyclopentadiene absorption is half as strong as that of cyclohexadiene, also as predicted in view of the different bond angles in the two rings. The absorption in both these molecules, begins, however, at abnormally long wave-lengths. This can be explained by