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Citation: *J. Chem. Phys.* **14**, 591 (1946); doi: 10.1063/1.1724071

View online: <http://dx.doi.org/10.1063/1.1724071>

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Notes on the Rate Process Theory of Flow*

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(Received March 11, 1946)

This paper deals with the separation of the contributing terms of the energy and entropy of activation for viscous flow and the identification of some of the molecular constants entering into these terms, as a step toward the prediction of the viscosity of liquids from first principles. The energy of activation for hole formation ΔH_t^h is found to be determined mainly by the magnitude of the dispersion energy and by the extent of displacement of the hole forming molecules from their equilibrium position. The latter, in the form of the viscosity-pressure coefficient ΔV_t , is, at present, not predictable from any molecular constant. The energy of activation for motion into the hole ΔH_t^i was found for many substances to be numerically equal to the excess energy of vaporization ΔE_{vap}^i and is thus an additional measure of restricted external rotation. The cases in which $\Delta H_t^i > \Delta E_{vap}^i$ offer strong evidence for the requirement of deformation of the flowing molecule against internal potential energy barriers. The rotational, translational, and cooperative terms which contribute to the entropy of activation have been separated, but can so

far be determined only from viscosity data. Numerical examples show that the stereometric arrangement of molecular structure determines the magnitude of ΔV_t and ΔH_t^i and thereby the viscosity of liquids to a far greater extent than chemical composition (except for OH groups). The existence of aliphatic fatty acids as double molecules in the liquid state over a wide range of temperatures is confirmed viscosimetrically, while the viscosity data of aliphatic alcohols suggest the presence of distinguishable multiple molecules only at very low temperatures but the existence of a continuous OH-bond network structure at ordinary temperatures. One of the important consequences of the rate process theory of flow is the recognition that the viscosity of a liquid is determined by the (very small) concentration of molecules in relatively shallow potential energy walls from which the activated molecules are preferentially recruited. Viscosity is therefore not a bulk property in the commonly accepted sense and depends only to a minor extent on the structure of a liquid, i.e., on its state of order.

THE object of this investigation was to separate the terms contributing to the energy and entropy of activation for viscous flow occurring in Eyring's¹ equation

$$\eta = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} \exp(-\Delta S_t/R) \exp(\Delta H_t/RT) \\ \sim \frac{Nh}{V} \exp(-\Delta S_t/R) \exp(\Delta H_t/RT)$$

(where $\lambda_{1,2,3}$ =intermolecular distances in the three space coordinates, λ =length of path over potential energy barrier, h =Planck constant, V =molar volume (used where $\lambda=\lambda_1$), ΔS_t =entropy of activation, and ΔH_t =heat of activation), in order to facilitate the prediction of the absolute value of the viscosity of liquids from first principles.

1. THE HEAT OF ACTIVATION ΔH_t

ΔH_t is also defined by

$$\Delta H_t = R \left(\frac{\partial \ln(V\eta)}{\partial 1/T} \right)_P \quad (1)$$

* Presented in part at the annual meeting of the Society of Rheology, New York, October 26, 1945.

¹ Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, New York, 1941). R. E. Powell, Ph.D. Thesis, Princeton (1943).

It has been suggested by Eyring¹ and his co-workers that ΔH_t consists of two elements: the energy required to form a hole in the liquid structure and the energy required to move into this hole. The latter is

$$\Delta H_t^i = R \left(\frac{\partial \ln \eta}{\partial 1/T} \right)_V, \quad (2)$$

so that the energy of hole formation is

$$\Delta H_t^h = \Delta H_t - \Delta H_t^i \\ = R \left\{ \left(\frac{\partial \ln(V\eta)}{\partial 1/T} \right)_P - \left(\frac{\partial \ln \eta}{\partial 1/T} \right)_V \right\}. \quad (3)$$

So far no inquiry has been made into the nature of either ΔH_t^h or ΔH_t^i . It is here proposed to derive the two parameters as follows: From the model underlying the rate process theory of flow we can deduce that ΔH_t^h is the change in potential energy between neighboring molecules accompanying the displacement from their equilibrium position when forming a new hole. The displacement can be computed from the pressure coefficient of viscosity, as

$$\left(\frac{\partial \Delta F_t}{\partial p} \right)_T = \Delta V_t, \quad (4)$$

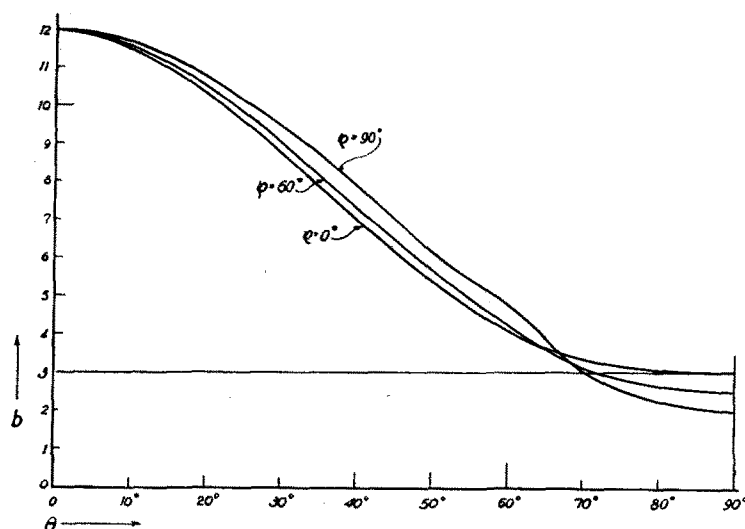


FIG. 1. London's orientation function.

$$b = 6 + 2.0(3 \cos^2 \theta - 1) + \{[(\sin \theta)^2 \cos \varphi - 2(\cos \theta)^2]^2 - 2 \cos^2 \theta\}$$

for various values of θ and φ .

$$-E^{11} = \frac{b I_0 \alpha^2}{4 r^6}; \text{ for } \alpha_{11} - \frac{\alpha_1}{a} = 1.$$

where ΔF^\ddagger = free energy of activation for viscous flow and ΔV^\ddagger = local volume change (increase) accompanying the process of activation. The linear displacement of the molecules forming a hole is, therefore, to a good approximation $(1/N^\ddagger)[(V + \Delta V^\ddagger)^\ddagger - V^\ddagger]$. Using Lennard-Jones² equation for the potential energy between a central molecule and its nearest neighbors we obtain for ΔH^\ddagger the expression

$$\Delta H^\ddagger = \Lambda^* \left\{ 1.2 \left[\left(\frac{V^*}{V} \right)^2 - \left(\frac{V^*}{V^\ddagger} \right)^2 \right] - 0.5 \left[\left(\frac{V^*}{V} \right)^4 - \left(\frac{V^*}{V} \right)^4 \right] \right\}, \quad (5)$$

where $\Lambda^* = Z\epsilon^*$, the minimum value of the interaction energy ϵ at the equilibrium distance r^* , Z = number of nearest neighbors, $V^* = r^{*3}/\sqrt{2}$, $V^\ddagger = V + \Delta V^\ddagger$, $\Lambda^* \sim 1.2\Delta E_{\text{vap}}$ in many cases. Inasmuch as (5) is based on London's inverse sixth power law for molecular interaction³ one can readily show that the magnitude of ϵ is determined by the factor $\frac{3}{4}I_0\alpha^2$ in the case of non-polar compounds and contains the additional term $(2/3)(\mu^4/kT)$ in the case of dipolemolecules, where I_0 = first ionization potential (also derivable from ultraviolet spectra⁴)

and α = polarizability. One could argue that Eq. (5) is valid only for spherical molecules or at least only for those of spherical fields of force and that a more complicated expression is required to describe the potential energy field of linear polyatomic molecules. London's recent equation for the dispersion energy in systems composed of linear molecules⁵ takes into consideration the difference in polarizability vertical to and in line with the bond axes. The potential energy between neighboring molecules becomes thus a function of their angle of approach. Figure 1 is a plot of the value of the numerical coefficient before $I_0\alpha^2$ as a function of the angles of approach. It is seen that the potential energy is at a minimum for parallel orientation of the bond axes, in agreement with the known x-ray diffraction patterns of *n*-paraffins and their derivatives. In calculating the potential energy along these curves, it becomes apparent that the difference in potential energy between the top and the bottom is of such magnitude that there should still be a finite concentration of molecules which are randomly oriented with respect to each other. This difference is often of the same order of magnitude as ΔF^\ddagger . As ΔF^\ddagger is defined by

$$\Delta F^\ddagger = RT \ln \left(\frac{V\eta}{Nh} \right) = -RT \ln \frac{c^\ddagger}{c}, \quad (6)$$

² Lennard-Jones and Devonshire, Proc. Roy. Soc. A163, 53 (1937); A165, 1 (1930).

³ F. London, Trans. Faraday Soc. 33, 8 (1937).

⁴ W. C. Price, *et al.* Nature 148, 372 (1942); Proc. Roy. Soc. A174, 207 (1940).

⁵ F. London, Surface Chemistry II (AAAS, 1943), p. 141.

where c_{\ddagger} and c are the concentration of the activated and normal molecules, respectively, it appears reasonable to deduce that the activated molecules are (preferentially) recruited from the randomly oriented molecules whose numerical factor in front of $I_0\alpha^2$ is so nearly equal to $\frac{3}{4}$ that the use of the simple Eq. (5) is fully justified for molecules of any shape, provided

$$\langle E_{\max}'' \rangle - \langle E_{\min}'' \rangle \lesssim \Delta F_{\ddagger}.$$

The close agreement of the values of ΔH_{\ddagger}^h calculated by Eqs. (5) and (3) indicates the validity of the assumptions made in the derivation of (5).

If we remember that the energy of vaporization is the energy required to make a hole of molecular size, we should expect the ratio $\Delta H_{\ddagger}^h/\Delta E_{\text{vap}}$ to be of the order of (or equal to) $\Delta V_{\ddagger}/V$. The data on Table I show this indeed to be the case, what *cannot* be said of the ratio $\Delta H_{\ddagger}/\Delta E_{\text{vap}}$ as has been proposed by Eirich and Simha⁶ and accepted by Eyring* and many subsequent workers. A number of cyclic-hydrocarbons and similarly constituted liquids show $\Delta H_{\ddagger}/\Delta E_{\text{vap}}$ values larger than 1,⁷ but their $\Delta V_{\ddagger}/V$ and $\Delta H^h/\Delta E_{\text{vap}}$ values are of the usual order of magnitude, i.e., around 0.2.

As I_0 , α , and V^* (and ΔH_V) can be determined independently of viscosity, ΔH_{\ddagger}^h of any liquid could be predicted if ΔV_{\ddagger} were also derived from first principles; this has, however, not yet been accomplished. But it is conceivable that one could achieve this aim on the basis of Alfrey's model of the flow process.⁸ The peculiar temperature dependence of ΔH_{\ddagger}^h (it goes through a maximum as does ΔV_{\ddagger}) is not immediately derivable from either Eqs. (5) or (7) and may well be connected with the anisotropic thermal expansion of the unit cells of a liquid, as observed by x-ray diffraction.⁹ Some specific cases of relationships between structure changes of a liquid and ΔH_{\ddagger} will be discussed later on.**

⁶ Eirich and Simha, J. Chem. Phys. **7**, 116 (1939).

* Eyring's other relation $\Delta E_{\text{vap}}/\Delta F_{\ddagger} = 2.45$ was purely fortuitous as it was observed in the course of this work that ΔF_{\ddagger} passes often through a minimum and rises then constantly until T_{crit} ; $\Delta E_{\text{vap}}/\Delta F_{\ddagger}$ taking on values ranging from 4 to 0.

⁷ A. Bondi, ACS-Meeting in print, 1945, Petroleum Division, p. 315.

⁸ T. Alfrey, Rheol. Bull. **16**, No. 1 (1945).

⁹ E. W. Skinner, Phys. Rev. **36**, 1625 (1930).

** The anomalous increase of ΔH_{\ddagger} with temperature which has so far mostly been observed for low boiling liquids (see $h-c_6$ on Fig. 5a, and the lower alcohols on

The other component of ΔH_{\ddagger} , the energy of motion ΔH_{\ddagger}^i has a number of interesting properties which point toward an understanding of its nature, and which have so far been entirely overlooked: (a) the strong temperature dependence and (b) the close relation between ΔH_{\ddagger}^i and the "non-ideal" portion of ΔE_{vap} .

The first named of these properties is peculiar to heats of activation connected with the activation of internal degrees of freedom.¹⁰ The number $S/2$ of degrees of freedom activated is to (a not very good)† approximation

$$-\left(\frac{\partial \Delta H_{\ddagger}^i}{\partial T}\right)_P = R\left(\frac{S}{2} - 1\right), \quad (8)$$

and the average characteristic frequency ν_{\ddagger} of these degrees of freedom could be given by

$$\Delta H_{\ddagger}^i = -\frac{S}{2} N h \nu_{\ddagger}. \quad (9)$$

The values of $S/2$ and ν_{\ddagger} thus calculated are assembled in Table II. One sees that $S/2$ increases quite regularly with molecular weight, as would be expected, and that ν_{\ddagger} is of the order of Raman shifts and infra-red bands ascribed to external and internal rotation.¹¹ The motion of larger molecules past each other seems to require the activation of normally (at that temperature)

TABLE I. The heat of activation for hole formation ΔH_{\ddagger}^h (in kcal./mole) calculated by Eqs. (3) and (5), and its relation to the energy of vaporization.

		ΔH_{\ddagger}^h from equation		ΔV_{\ddagger}	ΔH_{\ddagger}^h	ΔH_{\ddagger}^h	ΔH_{\ddagger}
	$^{\circ}\text{C}$	(3)	(5)	V	ΔE_V^*	ΔE_V	ΔE_V
CCl_4	0/30	1.700	1.06	0.188	0.244	0.237	0.34
<i>n</i> -hexane	0/30	0.715	0.61	0.136	0.105	0.100	0.21
<i>n</i> -octane	0/30	0.860	0.66	0.100	0.101	0.090	0.20
<i>n</i> -decane	0/30	0.900	0.80	0.099	0.097	0.090	0.25
Toluene	0/30	1.352	1.00	0.135	0.165	0.155	0.23
<i>n</i> -propanol	0/30	0.970	1.60	0.209	0.130	0.090	0.38
<i>n</i> -pentanol	0/30	1.440	1.60	0.192	0.168	0.115	0.46
Oleic acid	0/30	2.99	2.80	0.106	—	0.125	0.24

$$* \Delta E_V^* = \Delta E_V - \Delta E_{Vi}.$$

Fig. 7) may also be connected with the fact that the concentration c_{\ddagger} of activated molecules starts in all of these cases to rise above about 1 percent in the same temperature range. Mutual interference of the activated zones may, therefore, be responsible for these peculiarities.

¹⁰ D. D. Eley, Trans. Faraday Soc. **39**, 168 (1943) and private communications.

† See discussion between R. M. Barrer and D. D. Eley in Trans. Faraday Soc. **39** (1943).

¹¹ G. Herzberg, *Molecular Spectra II* (D. Van Nostrand Company, New York, 1945), p. 496 seq.

TABLE II. The internal energy contribution ΔH_i^j to the energy of activation for viscous flow.

	ΔH_i^j kcal./m	at °C	ΔH_i^j kcal./m	at °C	ΔE_V^j kcal./m	S/2	$\bar{\nu}$ cm ⁻¹
Neo-pentane	0.690	30/50	0.0	50/100	0.000	10.0	12
<i>n</i> -hexane	0.805	0/30	0.570	40/75	0.450	3.8	63
<i>n</i> -octane	1.060	0/30	0.670	40/75	1.040	5.6	54
<i>n</i> -decane	1.610	0/30	1.250	40/75	0.740	5.2	96
Benzene	0.462	0/30	0.0	50/75	0.355	5.3	30
<i>O</i> -xylene	0.695	0/30	0.115	60/75	—	6.5	23
Methyl alcohol	1.810	0/30	1.650	40/75	2.030	2.9	212
Ethyl alcohol	2.430	0/30	—	—	2.340	—	—
<i>n</i> -propyl alcohol	3.200	0/30	2.850	40/75	3.320	5.1	207
<i>n</i> -amyl alcohol	3.910	0/30	3.550	40/75	3.670	5.2	251
Acetone	0.570	0/30	0.400	40/75	0.730	2.0	85
Carbon tetrachloride	0.660	0/30	0.433	40/75	0.195	3.7	52
Ethyl iodide	0.780	0/30	0.635	40/75	0.870	2.7	92

TABLE IIA. Values of ΔH_i^j , ΔH_i^h , ΔH_i^k and $\Delta V_i^j/V$ of several petroleum-fraction (lubricating oils).

Oil	t °C	ΔH_i^\dagger kcal.	ΔH_i^{ij} kcal.	$S/2$	$\bar{\nu}$ cm ⁻¹	n	ΔH_i^h kcal.	$\frac{\Delta H_i^h}{\Delta E_V}$	$\frac{\Delta V_i^\dagger}{V}$
A-285	38/54	8.0	4.0	26	43	21	4.0	0.180	0.181
	54/99	6.30	2.43				3.87	0.180	0.120
A-409	38/54	14.80	7.11	31	68	30	7.69	0.235	0.163
	54/99	11.30	5.22				6.08	0.190	0.145
N-364	38/54	7.90	3.93	18	64	26	3.97	0.145	0.160
	54/99	6.77	2.87				3.90	0.146	0.100
N-393	38/54	10.50	5.48	32	49	29	5.02	0.167	0.167
	54/99	7.80	3.54				5.21	0.185	0.109
N-435	38/54	11.63	5.82	24	78	32	5.81	0.177	0.169
	54/99	9.44	4.43				5.01	0.160	0.126
N-666	38/54	12.80	7.63	42	53	48	5.17	0.125	0.087
	54/99	10.30	5.18				5.14	0.130	0.079
Waterman analyses of oils used:				A-285	A-409	N-364	N-393	N-435	N-666
Rings per molecule				2.18	3.45	2.48	2.75	3.13	3.40
C-atoms in paraffin side chains				11	15	15	17	19	34

Notes: n = average number of C-atoms per molecule (note the fairly good proportionality between n and $S/2$). ΔE_V was estimated from the heat of evaporation data of "similar" pure hydrocarbons and corrected to the temperature of viscosity measurement using $\Delta C_p(\text{liq-gas}) = 0.2 C_p \text{ liq.}$ which has been found a rather good approximation, for hydrocarbons of this molecular weight range.

The constants of this table have been computed from viscosity data by R. B. Dow, J. S. McCartney, and C. E. Fink, J. Inst. Petr. 27, No. 213, 301 (1941).

still unexcited external rotation and sometimes even internal rotation, i.e., actual deformation of the molecule. There seems to be a way to differentiate between the two, and this involves the second of the properties of ΔH_i^j mentioned above, the relationship to the non-ideal portion of the energy of vaporization. According to Hildebrand¹² the ideal entropy of vaporization at a vapor concentration of 0.0202 mole/l is 20.2 e.u. The excess entropy of vaporization ΔS_V^j leads to the non-ideal portion of the energy of

vaporization ΔE_V^j by

$$\Delta E_V^j = T(\Delta S_{\text{vap}} - 20.2) = T\Delta S_V^j. \quad (10)$$

Table II contains a number of ΔE_V^j values, compared—where the Hildebrand-temperature falls within the range of the viscosity measurements—with ΔH_i^j . The close similarity between ΔH_i^j and ΔE_V^j is quite striking. Some of the inconsistencies in the homologous series are probably caused by inaccurate viscosity and/or vapor pressure data.

¹² J. H. Hildebrand, J. Chem. Phys. 7, 233 (1939).

If we accept the suggestion by Halford¹³ that ΔS_v^i is closely related to the length of free swing required for rotational motion in a liquid, we may say that whenever $\Delta H_v^i \leq \Delta E_v^i$ the activated rotation is a normally unexcited or restricted external rotation.* When $\Delta H_v^i > \Delta E_v^i$ as in the case of neo-pentane and other more complex hydrocarbons, we must assume ΔH_v^i to be caused by the activation of internal rotations, i.e., of the individual motion of molecule segments past (internal) potential energy barriers. As restricted internal rotation would hardly be affected by change from the liquid to the gaseous state, it would not contribute to ΔS_{vap} .

In either case ΔH_v^i arises from insufficiency of the available free volume for the molecule to execute free rotational motions. Considering that ΔH_v^i decreases to zero for non-polar substances at elevated temperatures, it appears reasonable to introduce the postulate that the molecules of

a liquid will encounter no obstacles to free motion wherever the effective free volume expanded to a certain fraction, V_f^0/V , of the molecular volume. It is here proposed to write, therefore

$$\Delta H_v^i = E_r \left\{ 1 - \left(\frac{\delta_3 V_f}{V_f^0} \right)^4 \right\}, \quad (11)$$

where E_r = energy of the restricted rotator, δ_3 = free angle ratio, V_f = free volume. Discussion of this equation is beyond the scope of this paper and will appear at a later date, suffice it to say that no unreasonable assumptions are required to give a good fit of the experimental data.

To sum up: ΔH_v^i is more complicated to derive from first principles than ΔH_v^h , and can in many (but not all) cases be predicted—for one temperature—from the excess entropy of vaporization. [Its temperature coefficient can in the case

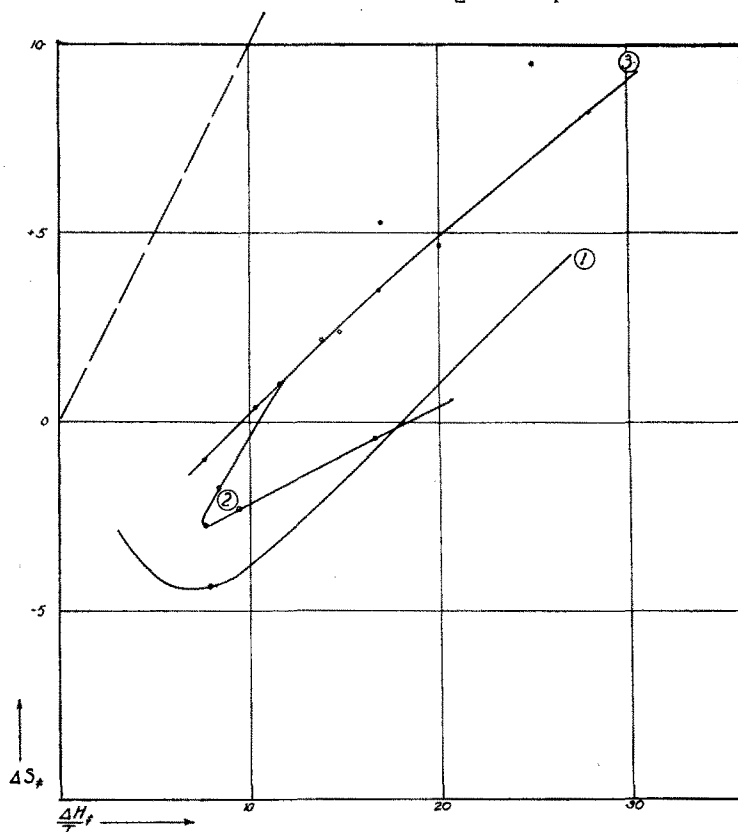


FIG. 2. Relation between ΔS_v and $\Delta H_v/T$ at $T = 303^\circ\text{K}$ for aliphatic hydrocarbons (1), alcohols (3), and acids (2). Slope of broken line = 1.0.

¹³ R. S. Halford, J. Chem. Phys. 8, 496 (1940).

* In this case Eq. (8) would either have to be thought of as applying to more than one molecule, or to be abandoned entirely.

of hydrocarbons be very approximately computed from the number of C-atoms per molecule.] Where strong dipole forces are active ΔH_f^\ddagger changes but little with temperature.

2. THE ENTROPY OF ACTIVATION

In most previous investigations little attention has been paid to the entropy of activation for viscous flow ΔS_f^\ddagger , since its numerical value deviates but little from zero for most of the "common" liquids. The more viscous materials which have been examined in the course of this study show, however, ΔS_f^\ddagger values of between -10 and $+100$ e.u. which cannot possibly be ignored. One can observe fluids of high ΔH_f^\ddagger to show also large ΔS_f^\ddagger values. There is, indeed, within any one group of compounds a degree of proportionality between ΔS_f^\ddagger and ΔH_f^\ddagger (Fig. 2) which reminds one of the Barclay-Butler rule¹⁴ connecting the heat and entropy of vaporization. Frank suggested¹⁵ that the Barclay-Butler rule has the following meaning: "When a vapor condenses, a molecule, so to speak, falls into a potential well, i.e., the greater the loss of energy on condensation, the narrower it is and the smaller the free volume, therefore the greater the loss of entropy. In addition, the deeper and narrower the well, the greater the interference tends to be, not only with moving back and forth, but also with squirming into different positions. This also means loss of entropy." Applying this to the process of activation for flow, we should expect the same partition function changes to contribute to ΔS_f^\ddagger which contributed to ΔH_f^\ddagger . The

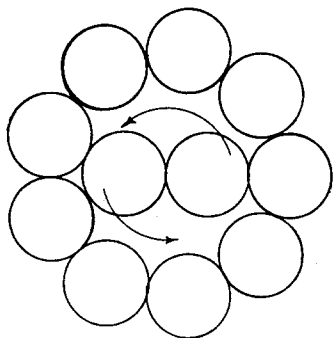


Fig. 3. Alfrey's model; rotational flow.

¹⁴ I. M. Barclay and J. A. V. Butler, *Trans. Faraday Soc.* **34**, 1445 (1938).

¹⁵ H. S. Frank, *J. Chem. Phys.* **13**, 793 (1945).

greater group specificity of the ΔS_f^\ddagger vs. ΔH_f^\ddagger relationship points to the existence of a factor, which is specific for the flow process and does not affect vaporization, the cooperation of molecule pairs as depicted by Alfrey's⁸ model of the flow (Fig. 3). The probability for two of the few molecules of extra energy content ΔH_f^\ddagger to collide and align "properly" for this minuet is certainly very small and bound to contribute a sizeable negative term to ΔS_f^\ddagger . This term and the term for intramolecular cooperation lumped together as $\Delta S_f^{\ddagger c}$ would be the only sources of entropy change once $\Delta H_f^\ddagger/T$ is zero. The intercept of the ΔS_f^\ddagger vs. $\Delta H_f^\ddagger/T$ curves with the ΔS_f^\ddagger axis would, therefore, be $\Delta S_f^{\ddagger c}$.

As would be expected, $\Delta S_f^{\ddagger c}$ is constant at low temperatures but increases at high temperatures reaching relatively quickly another constant value, which is then identical with ΔS_f^\ddagger , suggesting that at elevated temperatures, the entire entropy change is caused by cooperative factors. Relationship between $\Delta S_f^{\ddagger c}$ and chemical constitution will be discussed later. Prediction of its magnitude by other than semi-empirical rules seems at present not possible.

Other terms contributing to ΔS_f^\ddagger are: $\Delta S_f^{\ddagger tr}$ which can be derived from the change in effective free volume and would be

$$\Delta S_f^{\ddagger tr} = R \ln \left(\frac{\delta_3 V_f + \Delta V_f^\ddagger}{\delta_3 V_f} \right);$$

$\Delta S_f^{\ddagger tr}$ contributes about 1.5 to 10 e.u. The higher values are associated especially with liquids composed of spherically shaped molecules, whose free volume is usually small and ΔV_f^\ddagger quite large. Another term is $\Delta S_f^{\ddagger rot}$, which is caused by the activation of external rotation. The origin of this rotational contribution, the lack of free swing, has been mentioned above in connection with ΔH_f^\ddagger . The same considerations which led to the conclusion (in Eq. (11)) that only a fraction of the total energy of a rotator has to be supplied for the process of activation, depending on the available free volume, apply to the magnitude of $\Delta S_f^{\ddagger rot}$. In addition we have to consider the possibility that the flow process might require rotation only around a single preferred axis. There is some experimental evidence for this hypothesis: If we compare the entropy of activation for dipole orientation $\Delta S_f^\ddagger(\epsilon)$ and for viscous

TABLE III. Comparison of the processes of activation for flow and for dipole orientation.

Substance	Process	<i>t</i> °C	ΔF^\ddagger kcal.	ΔH^\ddagger kcal.	ΔS^\ddagger e.u.	$\Delta S^\ddagger(\epsilon) - \Delta S^\ddagger(\eta)$ e.u.	$S(\text{rot} - I)^{**}$ e.u.
<i>n</i> -propanol	Flow	25	3.52	4.53	3.4		
	Orientation	25	3.57	6.10	8.5	5.11	6.7
<i>n</i> -butanol	Flow	25	3.79	4.61	2.75		
	Orientation	25	3.90	6.40	8.4	5.65	8.2
Cocoanut oil	Flow	30	6.67	6.71	0.15		
	Orientation	30	2.26	8.16	19.4	19.25	22.7
Ethyl abietate	Flow*	10	8.24	23.84	55.0		
		10	4.18	26.30	78.0	23	23.7
	Orientation	20	7.85	19.15	38.6	12.4	
		20	3.67	18.60	51.0		

* Extrapolated viscosity data used.

** Rotational entropy contribution calculated for rotation around longest axis of molecule.

flow $\Delta S^\ddagger(\eta)$, we shall find $\Delta S^\ddagger(\epsilon) - \Delta S^\ddagger(\eta)$ often to equal just the rotational entropy contribution calculated for rotation of the dipole around the longer axis of the molecule (see Table III), a motion which is in accord with our present views of the rotation of dipoles in an alternating electric field. Had $\Delta S^\ddagger(\eta)$ contained the complete ΔS^{rot} , $\Delta S^\ddagger(\epsilon)$ would have been smaller than $\Delta S^\ddagger(\eta)$ instead of larger, as is always observed. Which of the three possible external rotations contributes to $\Delta S^\ddagger(\eta)$ will for the time being be a matter of trial calculations.** As our knowledge of the small (difficultly observed) temperature dependent rotational Raman-shifts of liquids increases we shall approach the possibility of predicting ΔS^{rot} from such spectrographic data. Similar reasoning applies to the computing of the contribution ΔS^i of activated internal rotation (or torsional oscillations).

From the relation

$$\Delta S^\ddagger = R \ln \frac{F^\ddagger}{F} + \frac{\Delta E^\ddagger_{\text{internal}}}{T}$$

follows that the slope of the curves in Fig. 4 represents the ratio of the change in internal energy (during activation) to ΔH^\ddagger . It is in accordance with the views expressed above that—by these curves— $\Delta E^{\text{int}}/\Delta H^\ddagger$ should tend to zero at high temperatures (high V_f/V ratios).

To sum up the results of this analysis of ΔS^\ddagger :

** From the work of Kauzmann and Eyring [J. Am. Chem. Soc. **62**, 3113 (1940)] it could be concluded that ΔS^{rot} of the moving segment of long linear molecules is of the order of 7 e.u.

It is found that of the many terms contributing to ΔS^\ddagger only a few can be separated, let alone be predicted. By analysis of viscosimetrically determined data one can separate the contribution of cooperation factors ΔS^\ddagger_c , and the translational term ΔS^\ddagger_{tr} . In the future ΔS^{rot} and ΔS^i may become predictable from Raman or infra-red spectra in the 10 to 100 cm^{-1} range.

We must admit that the analysis of ΔH^\ddagger and ΔS^\ddagger which—it is believed—has here been tried for the first time has failed of its objective, the prediction of the absolute value of the viscosity of pure liquids from available physical property data, but the results obtained appear to provide sufficient new insight into the mechanism of the flow process to evaluate profitably the influence of molecular structure upon viscosity.

In the following paragraphs the influence of the two most prominent factors, molecular geometry and hydrogen bonding, upon ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger will be discussed in some detail.

3. MOLECULAR GEOMETRY AND VISCOSITY

A number of investigators have tried to calculate the viscosity or the viscosity-temperature coefficient from atomic or bond increments in a manner similar to the molar volume, parachor, refraction, etc.¹⁶ If it was not already obvious to a large number of workers in the field, the vast

¹⁶ E. C. Bingham and collaborators, J. Rheol. **1**, 372 (1930); **3**, 113, 479 (1932). J. N. Friend, Phil. Mag. **34**, 643, 810 (1943); **35**, 57, 136 (1944). H. Umstatter, Kolloid Zeits. **102**, 232 (1943). Others reviewed in "1st and 2nd Report on Viscosity and Plasticity to the Amsterdam Acad. Sci.," Amsterdam, 1935 and 1938.

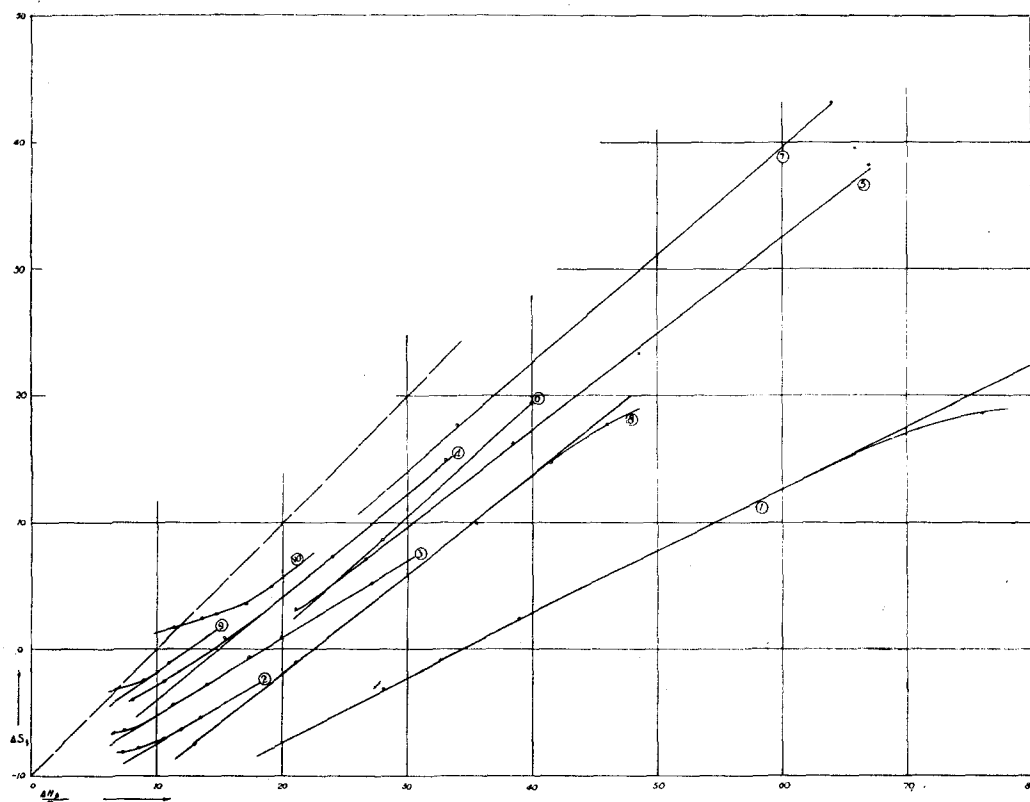


FIG. 4. Plot of ΔS^\ddagger vs. $\Delta H^\ddagger/T$ over a wide temperature range for a number of typical compounds. Slope of broken line = 1.0.

- ① Polyiso-butylene
- ② *n*-triatetracontane
- ③ 10-nonyl nonadecane
- ④ di-isobutyl-naphthalene
- ⑤ tri-(cyclohexyl-ethyl)-methane

- ⑥ tri cresyl phosphate
- ⑦ 2,2-di-pseudo cumente-propane
- ⑧ castor oil
- ⑨ cutyric acid
- ⑩ *n*-amyl alcohol

amount of viscosity data of pure hydrocarbons which have accumulated during the past decade¹⁷ has made it quite clear that these attempts have been futile. The various isomers of the hydrocarbon differ often in viscosity to such an extent that bond additivity is ruled out entirely.

On examining the equations of the previous sections for the basic causes of this behavior of liquids, we find that there are, indeed, a number of bond or atom additive properties contained in a number of parameters: the polarizability α in ΔH^\ddagger , the mass per molecule in the rotational energy and δ_3 , of ΔH^\ddagger and ΔS^\ddagger_{rot} and lastly the molar volume in the quotient Nh/V . There are, however, a number of decisive factors which are

¹⁷ See in M. P. Doss, *Physical Constants of the Principal Hydrocarbons* (Texaco, New York, 1943).

TABLE IV. Relationship between the volume requirement ΔV^\ddagger of the activated molecule and molecular structure (all from viscosity/pressure data below 1000 atmospheres).

Substance	<i>t</i> °C	ΔV^\ddagger cm ³	$\frac{\Delta V^\ddagger}{V}$	<i>t</i> °C	ΔV^\ddagger cm ³	$\frac{\Delta V^\ddagger}{V}$
(a) Flexible structures						
<i>n</i> -decane	30	18.4	0.094	75	14.3	0.072
di- <i>n</i> -amyl ether	30	21.7	0.106	75	21.7	0.102
<i>n</i> -octadecyl alcohol	70	29.2	0.087	150	33.3	0.092
Oleic acid	30	33.0	0.106	75	29.0	0.092
Oleyl oleate	20	38.6	0.064	—	—	—
Linseed oil	20	25	0.026	50	23	0.024
Castor oil	25	26	0.027	100	23.6	0.024
Petroleum fractions*						
N-393	38	72	0.167	99	49	0.114
N-670	38	65	0.087	99	61	0.079
(b) Rigid structures						
Neo-pentane	31	34.4	0.285	101	43.4	0.312
Cyclohexane	30	—	—	75	26.6	0.230
Chlorobenzene	30	13.2	0.128	75	14.8	0.138
Tetrachlorodiphenyl	54	116	0.582	99	44	0.218
Pentachlorodiphenyl	54	226	1.090	99	70	0.330

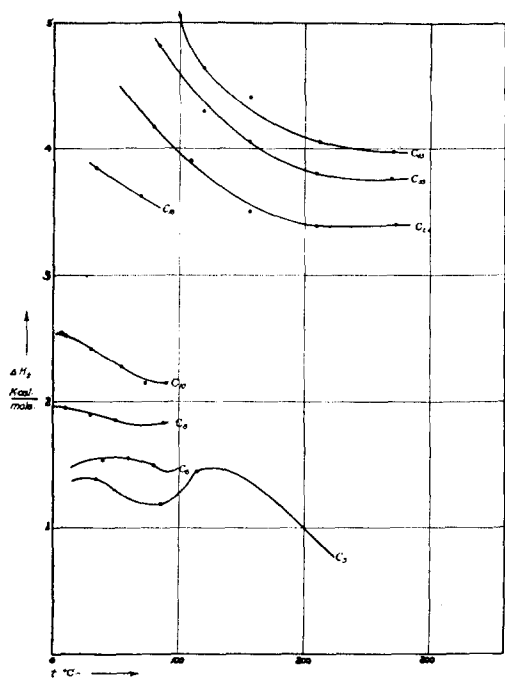
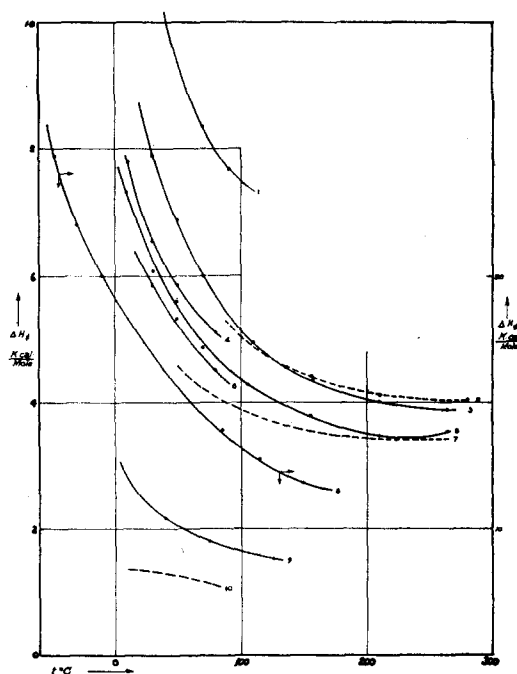
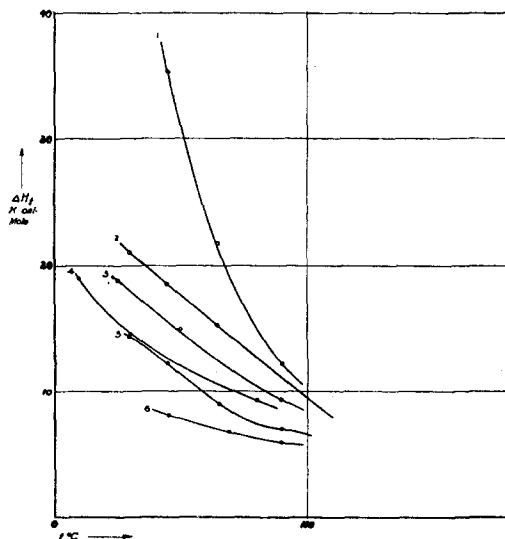
TABLE V. Effect of spatial configuration on viscosity of hydrocarbons and organo silicone derivatives.

	T °C	η poise	ΔH^\ddagger kcal.	ΔS^\ddagger e.u.	ΔV^\ddagger cm ³	$\frac{\Delta V^\ddagger}{V}$
<i>n</i> -pentane ($\Delta S_f = 14.0$ e.u.)	30 75	0.0022 0.00148	1.30 1.10	-4.0 -4.6	15.3 17.5	0.132 0.138
Neo-pentane ($\Delta S_f = 2.4$ e.u.)	30 100	0.0023 0.0011	2.20 1.80	-1.2 -2.5	34.4 43.4	0.285 0.312
<i>n</i> -hexane ($\Delta S_f = 17.5$ e.u.)	30 75	0.0029 0.0019	1.50 1.48	-4.2 -4.2	17.3 20.3	0.131 0.144
Neo-hexane	20	0.00375	1.70	-3.8	—	—
Ethyl-trimethyl-Silane*	20	0.00334	1.63	-4.0	—	—
Cyclo-hexane ($\Delta S_f = 2.2$ e.u.)	30 75	0.0082 0.0043	~ 2.68 ~ 2.68	~ -2.0 ~ -2.0	— 26.6	— 0.230
<i>n</i> -decane ($\Delta S_f = 28.3$ e.u.)	30 60	0.00783 0.0054	2.52 2.96	-3.5 -4.3	18.4 —	0.094 —
Cyclodecane	20 60	0.0448 0.0176	4.71 4.01	+1.1 -1.1	— —	— —
Decamethyl tetrasiloxane**	25 99	0.0131 0.00541	2.25 2.45	-6.5 -5.9	— —	— —
Octamethyl cyclo tetrasiloxane**	25 99	0.0220 0.0070	3.18 3.25	-4.1 -4.0	— —	— —
<i>n</i> -C ₂₆	60	0.0656(S)	4.32	-4.3	—	—
$\begin{array}{c} \text{C}_2 - \text{C} - \text{C}_{21} \\ \\ \text{C}_2 \end{array}$	20 60	0.20(S) 0.066(S)	5.50 4.43	0 -4.0	— —	— —
$\begin{array}{c} \text{C}_8 - \text{C} - \text{C}_8 \\ \\ \text{C}_8 \end{array}$	20 60	0.160(S) 0.050(S)	5.87 4.42	1.0 -3.34	— —	— —
$\left[\text{Cyclohexane} - \text{C}_2 \right]_3 \cdot \text{C}$	20 60	7.30(S) 0.45(S)	19.01 9.35	38.4 7.2	— —	— —
<i>n</i> -C ₃₂	80	0.099(S)	4.37	-6.1	—	—
(C ₁₀) ₃ · C	20 80	0.291(S) 0.055(S)	6.56 5.06	1.8 -3.03	— —	— —
$\begin{array}{ccccccc} \text{C}_6 & - & \text{C} & - & \text{C} & - & \text{C} \\ & & & & & & \\ \text{C}_2 & & \text{C}_6 & & \text{C}_6 & & \text{C}_2 \end{array}$	20 80 245	0.484(S) 0.063(S) 0.0079(S)	7.87 6.00 3.89	5.2 -0.6 -5.9	— — —	— — —

* Viscosity data from: F. C. Whitmore *et al.*, J. Am. Chem. Soc. **68**, 475 (1946).** Viscosity data from: C. B. Hurd, J. Am. Chem. Soc. **68**, 364 (1946), and D. F. Wilcock, *ibid.* **68**, 691 (1946).

not at all bond additive: ΔV^\ddagger , which determines the magnitude of ΔH^\ddagger , depends upon the flexibility of the molecule, and is the smaller a fraction of the total molecular volume the more flexible a molecule, that is, the smaller a molecular segment can move freely and act as unit of flow. Table IV gives a number of typical examples for the relationship between molecular structure and the value of ΔV^\ddagger . Attention is called to the extreme values for rigid spherical

structures like the chlorinated diphenyls on the one hand and the uniformly small ΔV^\ddagger of the linear molecules such as the fixed oils on the other. A remarkable feature of the important ratio $\Delta V^\ddagger/V$ is its independence from the constituent atoms of the molecule, being a function only of the relative distribution in space (*Raumerfuellung*) and—as mentioned above—of the flexibility of a molecule's structure. The non-additive elements of ΔH^\ddagger are E_r and δ_3 , which

FIG. 5a. *n*-paraffins. ΔH^\ddagger vs. temperature curves.FIG. 5b. ΔH^\ddagger vs. temperature curves of iso-paraffins. (Broken lines = *n*-paraffins for comparison.)FIG. 5c. ΔH^\ddagger vs. temperature curves of polycyclic hydrocarbons.

- ① 2, 2 dipseudo cumene propane
- ② β -dihydro diamyl anthracene
- ③ β -dihydro dioctyl anthracene
- ④ tri(ethyl cycloheptane) methane
- ⑤ β -dihydro diethyl anthracene
- ⑥ tri-octadecyl-benzene (for comparison)

- ① 7, 17 dimethyl, 9, 11, 13, 15 tetra hexyl eicosane
- ② 7, 12 dimethyl, 9, 10 dihexyl octadecane
- ③ *n*-tritetracontane
- ④ 11 decyl-heneicosane
- ④ 10-nonyl-nonadecane
- ⑤ 9-octyl-heptadecane
- ⑦ *n*-tetracosane
- ⑧ polyisobutylene
- ⑨ neopentane
- ⑩ *n*-pentane

FIG. 5. The temperature curves of the heat of activation ΔH^\ddagger . These curves show quite well the dependence of the temperature sensitive component of ΔH^\ddagger ; namely, ΔH^\ddagger_i , upon molecule size and structural complexity.

TABLE V(A). Effect of position of ring on viscosity.

	t °C	Viscosity stokes	ΔH_f^\ddagger kcal.	ΔS_f^\ddagger e.u.
<i>n</i> -octadecane (for comparison)	20	0.0579	3.84	-3.0
	80	0.0184	3.64	-3.8
1-phenyl dodecane	20	0.0629	4.36	-1.6
	80	0.0197	3.52	-4.1
2-phenyl dodecane	20	0.0688	4.74	-0.4
	80	0.0197	3.82	-3.2
4-phenyl dodecane	20	0.0782	5.40	+1.0
	80	0.0196	3.85	-3.2
6-phenyl dodecane	20	0.0880	5.94	+3.5
	80	0.0197	4.30	-1.9

contain the moments of inertia—and their product—being clearly determined by the relative distribution of the molecular structure in space, and the free volume V_f “which is due to the thermal displacements of the center of gravity of the molecule from its equilibrium position.”¹⁸ The free volume is thus directly related to the expansion at the melting point; the curious relationship between viscosity functions and the entropy of fusion ΔS_f becomes thereby somewhat clarified. The data on Table V show that whenever ΔS_f is large, ΔH_f^\ddagger and ΔS_f^\ddagger are small and *vice versa*. The behavior of the spherical molecules neo-pentane and cyclohexane—whose ΔS_f has nearly the theoretical value R

—is quite characteristic of this general trend. In other words V_f is—by ΔS_f and ΔV_f —also essentially a function of molecular geometry and not of chemical character.[†] The temperature coefficient of ΔH_f^\ddagger —and thereby of ΔH_f^\ddagger —is according to Eq. (11) determined by the expansion coefficient and V_f . The former is within any one group of compounds proportional to the reciprocal molecular weight, and varies quite generally inversely as the cohesive energy E'' .

These relationships are well recognizable in Figs. 5a-c.

The effect of most dipoles, excepting OH and NH, on ΔH_f^\ddagger and on viscosity in general, is quite small. This is not at all surprising for the size of the dipole interaction terms occurring in both ΔH_f^\ddagger and ΔH_f^\ddagger depends very strongly on the distance between the dipoles. With the exception of those dipoles which contain hydrogen this distance of closest approach is so large as to reduce the magnitude of the dipole interaction contribution to but a few hundred cal./mole, as is readily seen on Table VI, where polar molecules and structurally similar hydrocarbons are compared with each other.* It appears from these data that one need not consider chemical characteristics at all if one wants to synthesize

TABLE VI. Demonstrating the relative independence of viscosity function from chemical composition and the dominating effect of molecular structure.

Substance	M	t °C	η poise	ΔF_f^\ddagger kcal.	ΔH_f^\ddagger kcal.	ΔS_f^\ddagger e.u.	μ^\ddagger d.u.	$N\mu^2/r^3$ kcal.
Di- <i>n</i> -amyl ether	158	20	0.0108	3.66	2.87	-2.7	1.2	0.3
<i>n</i> -undecane	156	20	0.0117	3.74	2.94	-2.8	0	
Methyl stearate	298	50	0.039	5.23	4.11	-3.5	1.8	0.6
<i>n</i> -heneicosane	296	50	0.037	5.25	4.00	-3.8	0	
di-ethylhexyl sebacate	428	38	0.115	5.87	5.10	-2.4	3.6	2.4
9-octyldocosane	422	38	0.115	5.95	5.15	-2.6	0	
Tricresyl phosphate	368	60	0.135	6.15	9.03	8.7	(4.3)	2.3
Tri(ethylbenzene) methane	329	60	0.106	5.97	8.73	8.3	0	
Ethylabietate*	330	40	1.41	7.26	15.30	25.6	1.8	0.6
Di-isoamyl dihydro-anthracene*	322	40	4.20	7.82	18.7	36	0.5	

* These two compounds differ somewhat in structure. A better hydrocarbon analog of ethylabietate could, however, not be found in the literature. The relatively close numerical values of their viscosity constant demonstrate quite well the material effect of rigid condensed tricyclic structures.

† The dipole moments are estimated values.

¹⁸ Kincaid and Eyring, J. Chem. Phys. 6, 620 (1938).

† The relation between ΔH_f^\ddagger and *Raumerfüllung*, i.e., the three-dimensionality of molecular structure, has first been discovered by J. Pirsch, Ber. 70, 12 (1937).

* It should also be noted that μ^2/r^3 is the negative value of the orientation energy contribution to E'' at full parallel orientation of the dipoles. This interaction term will tend to zero with increasing angle of mutual orientation. As there is obviously always a finite (and quite sizeable) concentration of non-oriented dipole molecules from which c_t would be recruited, the influence of dipoles on viscosity is, as a rule, quite small; as is brought out by the figures above.

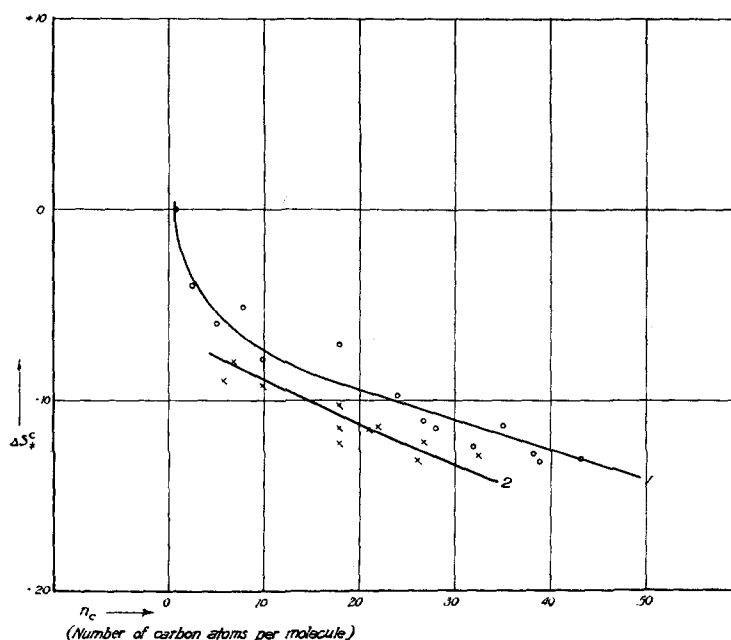


FIG. 6. Relationship between ΔS_{\ddagger}^c (from ΔS_{\ddagger} vs. $\Delta H_{\ddagger}/T$ intercept) and molecule size for long chain hydrocarbons (1) and cyclic hydrocarbons (2).

a substance of given viscosity characteristics but only the stereometric arrangement of molecular structure (provided there are no OH groups and not too many cumulative dipoles in the molecule).

The cooperative entropy factor ΔS_{\ddagger}^c is seemingly directly proportional to the size of the unit of flow (OH compounds excepted), Fig. 6. The balance of the entropy terms depend on the same factors as the corresponding energy contribution.

4. HYDROGEN BONDED LIQUIDS

The well-known anomalies caused by hydroxyl groups, which have been quite conclusively ascribed to hydrogen bonds¹⁹ are naturally also reflected in the viscosity function. The simplest case is represented by the fatty acids. Electron diffraction and vapor pressure data^{20, 21} have now well established that the hydrogen bond, coupling two carboxylic acids to a dimer unit, is so well stabilized (by resonance) that the double molecules exist not only in the liquid but even in the vapor state, at least for the lower members of the

fatty acid series. It is, therefore, but an additional confirmation of the reality of the double molecule to find that the viscosity parameters of fatty acids correspond remarkably well to those of hydrocarbons of the structure and molecular weight of the fatty acid double molecule, as seen from Table VII. Because of the relatively large accumulation of dipoles in the double molecule of the lower members of the series, the viscosity, ΔH_{\ddagger} , and ΔS_{\ddagger} of the latter are somewhat higher than would otherwise be expected. The consequently more pronounced contribution of the dipole interaction terms to ΔH_{\ddagger}^h and ΔH_{\ddagger}^i cause the quite small temperature coefficient of ΔH_{\ddagger}

TABLE VII. Evidence for the existence of fatty acids as double molecules by comparison of viscosity data with those of hydrocarbons and esters.

	<i>M</i>	<i>t</i> °C	η poise	$\Delta F_{\ddagger}^{\ddagger}$ kcal.	$\Delta H_{\ddagger}^{\ddagger}$ kcal.	$\Delta S_{\ddagger}^{\ddagger}$ e.u.
Propionic acid	(148)	20	0.011	(3.60)	2.45	(-3.8)
Propionic anhydride	130	20	0.011	3.51	2.66	-2.8
<i>n</i> -decane	142	20	0.0091	3.54	2.52	-3.5
Valeric acid	(204)	20	0.022	(4.28)	3.90	(-2.9)
<i>n</i> -tetradecane	198	20	0.022	4.22	3.44	-2.6
<i>n</i> -heptylic acid	(260)	20	0.043	(4.88)	4.04	(-2.9)
<i>n</i> -octadecane	254	20	0.045	4.78	3.95	-2.8
Oleic acid	(564)	20	0.318	(6.60)	5.90	(-2.3)
Oleyl oleate	532	20	0.330	6.30	5.30	-3.4

Data in parentheses are calculated for the double molecule.

¹⁹ S. Gladstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, New York, 1943), p. 114.

²⁰ J. Karle and L. O. Brockway, *J. Am. Chem. Soc.* **66**, 574 (1944).

²¹ H. L. R. Ritter and J. H. Simons, *J. Am. Chem. Soc.* **67**, 757 (1945).

TABLE VIII. Energies and entropies of activation of aliphatic alcohols.

	t °C	ΔH_t^\ddagger kcal.	$\Delta H_t^{\ddagger h}$ kcal.	$\Delta H_t^{\ddagger i}$ kcal.	ΔE_{Y^i} kcal.	$S/2$	ΔS_t^\ddagger e.u.	$\frac{\Delta V_t^\ddagger}{V}$	$\frac{\Delta H_t^{\ddagger h}}{\Delta E_{Y^0}}$
Methyl OH	15	2.20	0.40	1.80	2.03	2.9	-1.0	0.199	0.063
	60	2.28	0.63	1.65			0.0	0.204	0.095
Ethyl OH	15	2.97	0.61	2.43	2.34		0	0.185	0.082
	60	3.29							
<i>n</i> -propyl OH	15	4.16	0.97	3.20	3.32	5.1	2.2	0.209	0.129
	60	4.05	1.25	2.85			2.2	0.219	0.178
<i>i</i> -propyl-OH	15	5.00	1.12	3.88	—	3.4	3.5	0.256	
	60	4.95	1.18	3.67			4.7	0.266	
<i>n</i> -butyl-OH	15	4.60	1.37	3.29	4.30?	1.4	2.3	0.202	0.158
	60	4.45	1.20	3.25			2.3	0.185	
<i>i</i> -butyl-OH	15	5.46					5.0	0.225	
	60	5.21					4.0	0.219	
tri methyl carbinol*	35	8.68			3.00		15.0		
	70	6.15					7.5		
<i>n</i> -amyl-OH	15	5.35	1.44	3.91	3.67	5.2	4.7	0.192	0.182
	60	5.01	1.45	3.55			3.1	0.199	
<i>n</i> -heptyl-OH	10	5.4			3.30		2.5		
	70	4.7					1.5		
tri-ethyl carbinol*	10	12.3					26.5		
	70	5.5					4.5		
<i>n</i> -octanol†	10	6.48					5.9		
	90	5.05					1.4		
4-methyl-heptanol-3†	10	3.50					0		
	90	2.56					-3.3		
1-octadecanol	85	6.92	2.79	4.13		14	2.8	0.087 at 70°C	
	140	4.78	2.41	2.37			-2.7	0.092 at 150°C	

Notes: ΔE_{Y^i} refers to temperature at which vapor conc. = 0.0202 mole/l $\Delta V_t^\ddagger/V$ is always taken at 30 and 75°C, respectively, except where noted otherwise $\Delta E_{Y^0} = \Delta E_Y - \Delta E_{Y^i}$.

* The extremely high values of ΔH_t^\ddagger and ΔS_t^\ddagger for the symmetrical trialkyl carbinols seem readily ascribed to the spherical shape of these compounds. But only viscosity pressure data—which are still sadly missing—will provide through ΔV_t^\ddagger , $\Delta H_t^{\ddagger i}$ and $\Delta H_t^{\ddagger h}$ values a full understanding of the mechanism of flow of such fluids.

† The data of these two isomers were inserted to show the interference of hydrocarbon radical structure with OH-network formation.

and thereby the bent ΔS_t^\ddagger vs. $\Delta H_t^\ddagger/T$ curves shown in Fig. 9. Progressive dissociation of the dimer with increasing temperature would affect those parameters in the same direction.

The state of molecular aggregation of alcohols is less well defined than that of the fatty acids. At ordinary temperatures the bond between hydroxyl groups is not strong enough to form distinguishable double molecules. They rather form a continuous network structure throughout the liquid phase. Contrary to ordinary dipole systems, for which the potential energy difference between the fully oriented and random configuration is usually less than 2 kcal., the hydroxyl group *network* is more probable than

randomness by a potential energy difference of more than 10 kcal.²²

The motion of *any* alcohol molecule involves, therefore, passage of OH-groups past each other. Since the displacement per jump is not larger than with other molecules, ΔV_t^\ddagger and $\Delta H_t^{\ddagger h}$ are of normal magnitude, Table VIII, but the motion in the strong fields requires a $\Delta H_t^{\ddagger i}$ considerably greater than that of molecules of comparable size. As "the jumping pairs" now have a pre-determined configuration, ΔS_t^\ddagger of (the lower) alcohols is not very important, and ΔS_t^\ddagger becomes relatively high, compensating the large ΔH_t^\ddagger value somewhat. The viscosity of alcohols is

²² H. Harms, Zeits. f. physik. Chemie **B43**, 257 (1939).

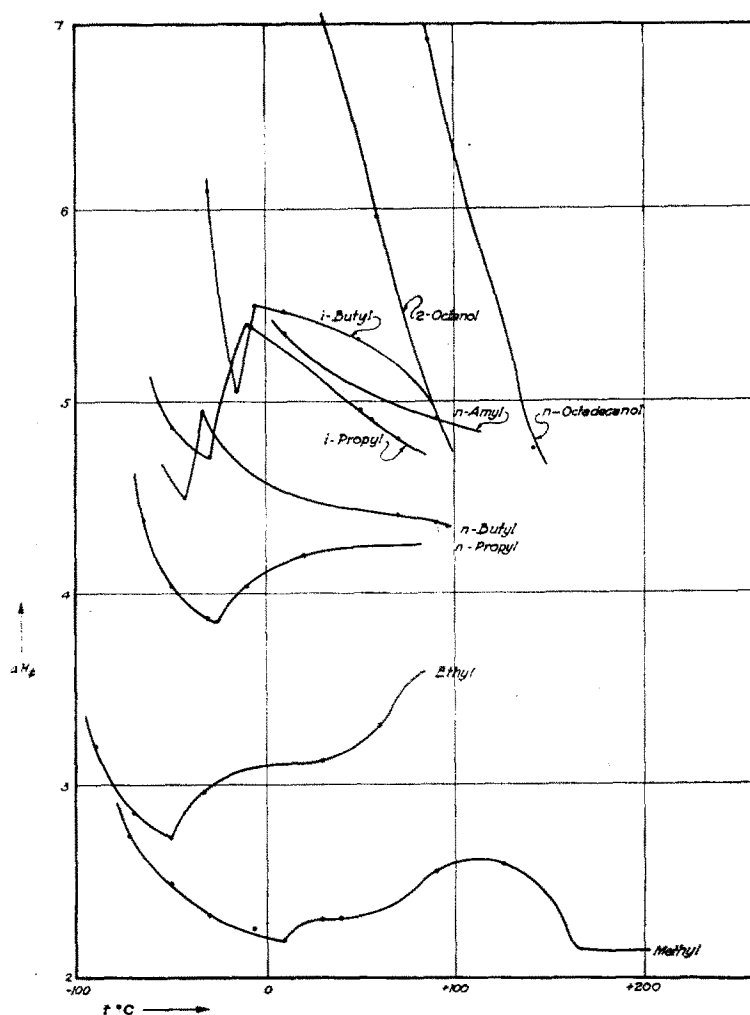


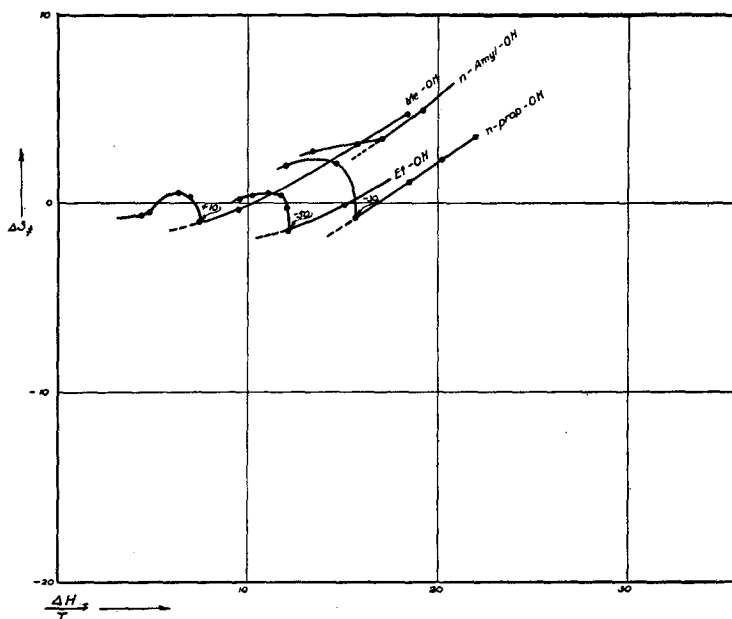
FIG. 7. ΔH^\ddagger vs. temperature curves of aliphatic alcohols.

nevertheless quite a bit higher than of other compounds of similar structure and molecular weight. Low temperature (at -75°C) x-ray diffraction data²³ indicate the presence of true hydrogen bridges (as in fatty acids) of 2.7 to 2.9 Å O—H—O distance in methyl and ethyl alcohols. At room temperature these are no longer observable. If this should mean that alcohols form distinguishable double or otherwise multiple molecules at low temperatures, whose motion would not involve mutual passage of OH-groups, one would expect ΔH^\ddagger to decrease at the same low temperature instead of increase. Calculation of ΔH^\ddagger from the careful viscosity

²³ G. G. Harvey, Phys. Rev. **55**, 1115 (1939).

measurements of Tonomura²⁴ down to -98°C shows this actually to be the case, as depicted on Fig. 7. Much more revealing, indeed surprising, are the ΔS^\ddagger vs. $\Delta H^\ddagger/T$ curves of these alcohols, shown in Fig. 8. They show the regular linear behavior at lowest temperatures until they reach a sudden inflection point, where within a fractional unit of $\Delta H^\ddagger/T$, ΔS^\ddagger increases by 1.6 to 3.0 e.u. Remembering that ΔS^\ddagger is in the form $e^{\Delta S^\ddagger/R}$ a measure of the population of a given energy state, we compute from these entropy changes that at the inflection point the number of units of flow (but not $c/c!$) increases (by

²⁴ T. Tonomura, Sci. Rep. Tohoku Imp. Univ. [1] **22**, 104 (1932).

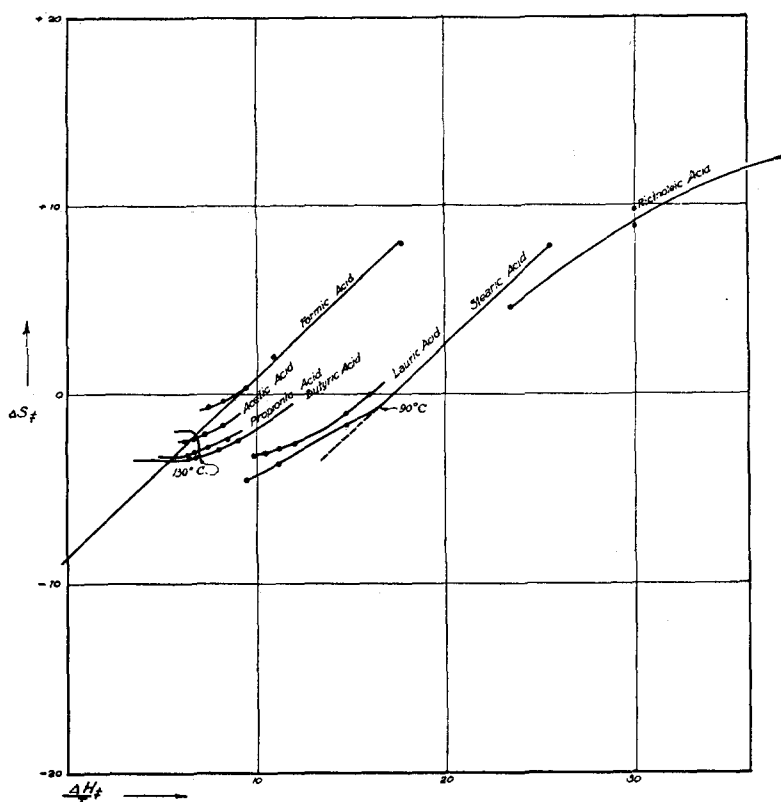
FIG. 8. Alcohols ΔS^\ddagger vs. $\Delta H^\ddagger/T$ curves.

increasing the temperature) by a factor of 2.2 for methyl-alcohol, 2.4 for ethyl alcohol, and 4.5 for *n*-propyl alcohol. The inflection temperatures are at about 10°C, -50°C and -30°C, respectively. The inflection of the butyl and amyl alcohol curves are more gradual, and less well defined. If the interpretation of the behavior of alcohols is correct, we should expect to observe similar effects of the dissociation of fatty acids upon ΔS^\ddagger and ΔH^\ddagger at elevated temperatures. There are but few high temperature viscosity data of fatty acids available, and dissociation of these in the liquid state takes place at temperatures at which the increase of ΔS^\ddagger starts already to flatten out the ΔS^\ddagger curves, but nevertheless the curves on Fig. 9 indicate the general trend to be as expected. Viscosity data of compounds containing more than one OH-group per molecule are very scarce. The most peculiar of these is castor oil. The ΔH^\ddagger values of this liquid, calculated from the viscosity data of Hersey and Shore²⁵ are presented on Table IX. The stepwise decrease of ΔH^\ddagger with increasing temperatures suggests successive disengagement of the hydroxyl groups with increasing disorder in the liquid.

²⁵ Hersey and Shore, *Mech. Eng.* **50**, 221 (1928).

5. VISCOSITY AND LIQUID STRUCTURE

The structure of liquids, which by x-ray diffraction and their theoretical interpretation has acquired the status of a reality today, has hardly been referred to in the quantitative discussion. It is, however, not accidental that the rate process theory of flow should be able to give a good account of the relationship between molecular structure and viscosity without explicit consideration of the structure of the liquid. The reason for this lies in the basic premise of the theory: the proportionality between fluidity and the concentration of activated molecules c^\ddagger . The smallness of c^\ddagger has never before been sufficiently emphasized. We have mentioned in Section 1 that c^\ddagger is small enough to be entirely recruited out of the small random oriented population even in such liquids, which are otherwise known as well-ordered systems, such as *n*-paraffins, fatty acids, etc. at ordinary temperatures. The activated molecules have since the inception of the theory been thought to occur only in the immediate neighborhood of lattice disturbances, the "holes." Just as the frequency of lattice imperfections in crystals is not *a priori* connected with the geometry of the lattice, such condition should

FIG. 9. Acids ΔS_{\ddagger} vs. $\Delta H_{\ddagger}/T$ curves.

not be expected to exist in liquids. An indirect connection does exist through the proportionality between the number of holes in the lattice and $\exp [(-\zeta^h + \zeta^i)/kT]$, where ζ^h is the energy of hole formation and ζ^i the potential energy of a molecule on an interlattice position, both of which are affected by the number of nearest neighbors and thereby the lattice arrangement. We shall similarly expect ΔV_{\ddagger} (and by it ΔH_{\ddagger}^h and ΔS_{\ddagger}^{tr}) to be affected by the number and arrangement of the nearest neighbors. Further refinement of the theory, designed to predict ΔV_{\ddagger} and its temperature and pressure function will, therefore, have to take the details of the liquid structure into account.

SUMMARY

1. The energy of activation for viscous flow consists of two independent terms: the energy of hole formation ΔH_{\ddagger}^h and the energy of motion into the hole ΔH_{\ddagger}^i . ΔH_{\ddagger}^h has here been derived as the change in potential energy between one

molecule and its nearest neighbors, which accompanies the displacement from equilibrium position incident to the formation of a hole. With the displacement given by the pressure coefficient of the free energy of activation $(\partial \Delta F_{\ddagger} / \partial p)_r = \Delta V_{\ddagger}$ London's interaction energy law is shown to predict ΔH_{\ddagger}^h values of the right order of magnitude. ΔH_{\ddagger}^i , the heat of activation of the viscosity isochore is shown to be often of the same magnitude as $T \times$ Hildebrand's excess entropy of vaporization, a parameter which might also be called the non-ideal portion of ΔE_{vap} . Both may be considered as a measure of restricted external rotation in the liquid state. Where ΔH_{\ddagger}^i is materially larger than ΔE_{vap}^i , the molecular structure as well as the temperature coefficient of ΔH_{\ddagger}^i suggest that the process of motion requires deformation of the molecule against internal potential energy barriers.

2. The entropy of activation ΔS_{\ddagger} is separated into a cooperative term ΔS_{\ddagger}^c which is derived graphically from the ΔS_{\ddagger} vs. $\Delta H_{\ddagger}/T$ curve, a

translational term ΔS_{\ddagger}^{tr} which is calculated from the volume increase ΔV_{\ddagger} and the free volume, and a rotational term $\Delta S_{\ddagger}^{rot}$, which represents the entropy counterpart of ΔH_{\ddagger}^i .

3. Numerical examples are provided to show that the viscosity of liquids depends largely on the stereometric arrangement of molecular structure and only secondarily on the nature of the constituent atoms and resulting dipole moments (OH groups excepted). This result is shown to be caused by the determining influence of the purely geometrical factor ΔV_{\ddagger} upon $\Delta H_{\ddagger}^{\ddagger}$ and ΔS_{\ddagger}^{tr} , and the presence of the product of the moments of inertia in ΔH_{\ddagger}^i and $\Delta S_{\ddagger}^{rot}$. These findings are believed to be significant for the planning of the syntheses of substances with given viscosity characteristics.

4. Viscosity data confirm the existence of fatty acids as double molecules in the liquid state at room temperature. The viscosity behavior of alcohols suggests the presence of distinguishable multiple molecules at low temperatures (below -50°C), and quite well-defined transition from this form to the continuous OH-bond network structure which prevails at ordinary temperatures.

5. It is pointed out that in all ordinary liquids the concentration c_{\ddagger}/c of activated molecules is

TABLE IX. ΔH_{\ddagger}^i values of castor oil.

$t^{\circ}\text{C}$:	20/40	40/60	60/80	80/100	100/133
ΔH_{\ddagger}^i kcal./mole:	8.75	8.28	5.33	5.34	2.60

so small (10^{-6} to 10^{-2}) that the random oriented portion of otherwise well-ordered liquids can usually provide their entire number. This causes—contrary to expectation—the structure of a liquid, i.e., its state of order, to play only a minor role in the calculation of viscosity.

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Where not noted otherwise, the constants inserted into the tables and figures of this paper have been computed from viscosity data by:

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