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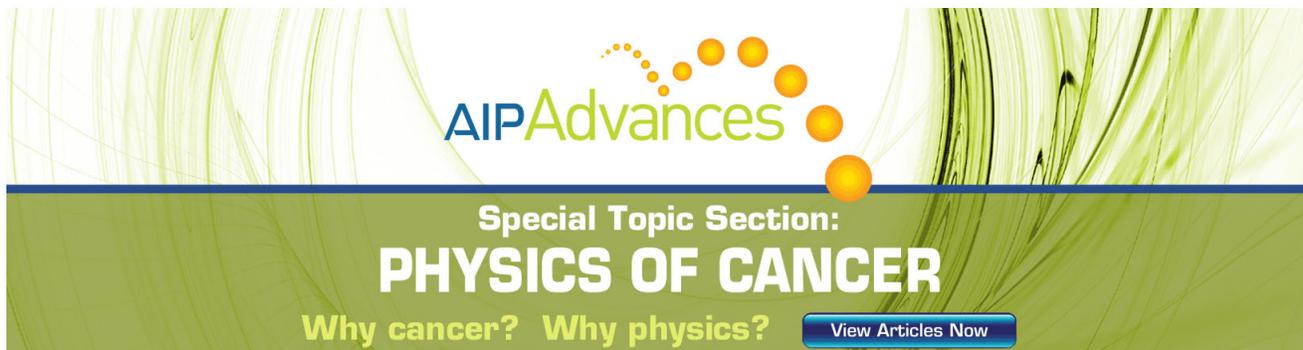
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Theory of the Viscosity of Liquids as a Function of Temperature and Pressure

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An equation for the viscosity of a liquid in terms of the energy of vaporization and the molal volume is developed from the reaction rate theory of viscosity due to Eyring. The degree of freedom corresponding to flow is assumed to be a translational one, and the energy of activation for the elementary flow process is assumed to be some fraction, $1/n$, of the energy of vaporization. On applying this equation to a large number of normal liquids it is found that molecules possessing spherical symmetry have $n=3$, while nonspherical molecules have n greater than 3, usually about 4. It is shown that the ratio

$$\Delta E_{\text{vap}}/\Delta E_{\text{vis}}, \text{ where } \Delta E_{\text{vis}} = R(d \ln \eta)/(d(1/T)),$$

can be taken as an index of the size and shape of the molecule, or more precisely, of the unit of flow in the liquid. The activation energy for flow in liquid metals is a very small fraction of the energy of vaporization, ranging from 1/10 to 1/25, leading to the conclusion that the metal ions flow

without their valence electrons. Viscosity data confirm the S_8 ring structure for sulfur below 160° and lead to the conclusion that above 250° sulfur probably consists of long chains containing as a rough average about 36 sulfur atoms. In the long chain hydrocarbons the activated configuration for flow is probably a curled up molecule. The structure activation energy of flow in associated liquids due to the hydrogen bond structure is discussed, and viscosity data are used to compute the degree of coordination in liquid water. At high pressures the energy of vaporization in the equation must be replaced by $V(p_{\text{internal}} + p_{\text{external}})$. This yields an equation for computing either the internal pressure of a liquid or the viscosity under pressure, if either is known. Using Bridgman's viscosity data, values of the internal pressures of some liquids are calculated from this equation which agree with internal pressures calculated from compressibility data.

BY considering viscous flow as a chemical reaction in which the elementary process is the passing of a single molecule from one equilibrium position to another over a potential barrier, Eyring¹ has developed the general equation:

$$\eta = \frac{\lambda_1 h}{\kappa \lambda^2 \lambda_2 \lambda_3} \frac{F_n}{F_a^*} \exp \frac{\Delta E_{\text{act}}}{kT}, \quad (1)$$

where

λ = distance between equilibrium positions in the direction of flow,

λ_1 = perpendicular distance between adjacent layers of molecules,

λ_2 = distance between adjacent molecules in the direction of flow,

λ_3 = distance between molecules in the plane of flow and normal to the direction of flow,

κ = transmission coefficient,

F_n = partition function of normal molecule,

F_a^* = partition function of the activated molecule, omitting the degree of freedom corresponding to flow,

ΔE_{act} = activation energy for the flow process.

κ is usually unity for chemical reactions and will

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

be so assumed in this development. If λ , the distance between equilibrium positions, is equal to λ_1 we have

$$\lambda_1/\lambda^2 \lambda_2 \lambda_3 = N/V,$$

where N is Avogadro's number and V is the molar volume.

If we assume that the degree of freedom corresponding to flow is a translational one and other degrees of freedom are the same for the initial and activated states:

$$\frac{F_n}{F_a^*} = \frac{\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V_f F_{\text{rot}} F_{\text{vib}}}{\frac{2\pi mkT}{h^2} V_f^{\frac{3}{2}} F_{\text{rot}} F_{\text{vib}}} = \frac{(2\pi mkT)^{\frac{1}{2}}}{h} V_f^{\frac{1}{2}} \quad (2)$$

where V_f = the free volume. Eyring and Hirschfelder² have formulated the free volume

$$V_f^{\frac{1}{2}} = \frac{bRT}{V^{\frac{3}{2}} N^{\frac{1}{2}} (p + a/V^2)} \text{ per molecule}$$

$$= \frac{bRT V^{\frac{1}{2}}}{N^{\frac{3}{2}} \Delta E_{\text{vap}}} \text{ if } \frac{a}{V^2} = \frac{\Delta E_{\text{vap}}}{V} \gg p, \quad (3)$$

where

² Eyring and Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937).

ΔE_{vap} = energy of vaporization = $\Delta H_{\text{vap}} - \Delta(pV)$
 $b = 2$ for simple cubic packing and has not very different values for other types of packing.

For a molecule to flow it must have a hole to flow into, but this may not necessarily have to be a hole the full size of a molecule. Therefore the activation energy for viscous flow will be some fraction of the energy of vaporization, $\Delta E_{\text{act}} = \Delta E_{\text{vap}}/n$, since ΔE_{vap} is the energy required to make a hole in a liquid the size of a molecule. Combining all these evaluations of the quantities in Eq. (1) we get

$$\eta = \frac{Nh}{V} \frac{(2\pi mkT)^{\frac{1}{2}} bRTV^{\frac{1}{3}}}{h N^{\frac{1}{3}} \Delta E_{\text{vap}}} \exp \frac{\Delta E_{\text{vap}}}{nRT}$$

$$= 1.090 \cdot 10^{-3} \frac{M^{\frac{1}{2}} T^{\frac{1}{2}}}{V^{\frac{1}{3}} \Delta E_{\text{vap}}} \exp \frac{\Delta E_{\text{vap}}}{nRT} \quad (4)$$

if we take $b = 2$, and R and ΔE_{vap} are in calories per mole.

In order to test Eq. (4) and for use elsewhere in this paper careful selections of density and heat of vaporization data were made from the values given in the Landolt-Börnstein *Tabellen*. In many cases it was necessary to plot the various values of the heats of vaporization against the temperature and draw a best straight line or curve through the points for interpolation purposes. E_{vap} was obtained from ΔH_{vap} by subtracting $\Delta(pV)$ of vaporization. The viscosity data used to test Eq. (4) and elsewhere in this paper were from the following sources:

Most organic liquids, Thorpe and Rodger, *Trans. Roy. Soc. (London)* **185A**, 307 (1894) and **189A**, 71 (1897), Timmermanns and co-workers, *J. chim. phys.* (1926-35).
 A, CH₄, N₂, CO, O₂, C₂H₄, Rudenko and Schubnikov, *Physik. Zeits. Sowjetunion* **6**, 470 (1934) and **8**, 179 (1935).
 C₉H₂₀, C₁₀H₂₂, C₁₁H₂₄, Bingham and Fornwalt, *J. Rheol.* **1**, 372 (1930).
 C₁₄H₃₀, C₁₆H₃₄, C₁₈H₃₈, Ubbelohde and Agthe, quoted in Engler-Höfer, *Das Erdöl* Vol. 1 (Berlin 1913), p. 53.
 Sulfur, Rotinjanz, *Zeits. f. physik. Chemie* **62**, 609 (1908).
 Na, K, Chiang, *Proc. Roy. Soc. (London)* **157A**, 264 (1936).
 Hg, Erk, *Zeits. f. physik. Chemie* **47**, 886 (1928).
 Ga, Spells, *Proc. Phys. Soc. (London)* **48**, 299 (1936).
 Ag, Zn, Cd, Gering and Sauerwald, *Zeits. f. anorg. allgem. Chemie* **223**, 204 (1935).
 Sn, Stott, *Proc. Phys. Soc. (London)* **45**, 530 (1933).
 Pb, Esser, Greis and Bungardt, *Arch. Eisenhüttenw.* **7**, 385 (1934).
 H₂O, *International Critical Tables* V, 10.

THE TEMPERATURE VARIATION OF VISCOSITY AND THE VALUE OF n

Using the data mentioned in the last section Eq. (4) was used to compute the viscosity of a number of liquids over a range of temperatures using half-integral values of n from 2 to 5. In order to ascertain which value of n gave the correct temperature coefficient, the computed values of the viscosity were plotted as $\log \eta$ against $1/T$. It is a well-known empirical fact that for all normal liquids $n = Ae^{B/T}$ where A and B are constant so that $\log \eta$ plotted against $1/T$ is a straight line. For any value of n the computed viscosities gave a $\log \eta$ vs. $1/T$ plot which was a straight line or in some cases very slightly convex towards the $1/T$ axis. The value of n which gave a plot parallel to the straight line of the observed viscosities was taken as the value of n which gave the correct temperature coefficient. These calculations were carried out for all the liquids for which fairly reliable heats of vaporization over a range of temperatures were known. The results to the closest half-integer are given in Table I. In most cases the $\log \eta$ vs. $1/T$ plot for the value of n given in Table I was nearly exactly parallel to the observed, and in a few cases where the plots were slightly divergent there was no doubt as to which was the closest half-integral value for n . As examples, Table II shows the calculations for CCl₄ and Fig. 1 shows the plots for CCl₄, N₂, C₆H₁₄, CHCl₃. Computations similar to Table II and plots similar to Fig. 1 were made for all the liquids listed in Table I.

TABLE I.

$n = 3$	CCl ₄ , C ₆ H ₆ , cyclohexane, CH ₄ , N ₂ , CO, A
$n = 3\frac{1}{2}$	C ₂ H ₄ Cl ₂ , C ₂ H ₄ Br ₂ , O ₂ *
$n = 4$	pentane, hexane, heptane, CS ₂ , CHCl ₃ , C ₆ H ₅ CH ₃ , ether, ethyl acetate, acetone, C ₂ H ₅ I, C ₂ H ₅ Br, CH ₃ I, C ₂ H ₄

* The anomaly of O₂ as compared to N₂ and CO may be attributed to its paramagnetic property. No explanation is offered for the result for the ethylene halides.

The fact that there is a sharp separation into two classes of liquids (except O₂, C₂H₄Cl₂, C₂H₄Br₂) with $n = 3$ and $n = 4$, respectively, is significant. Most of the $n = 3$ liquids have spherical or approximately spherical fields of force. This is certainly true of CCl₄, CH₄ and A, and is very nearly true of N₂ and CO when the

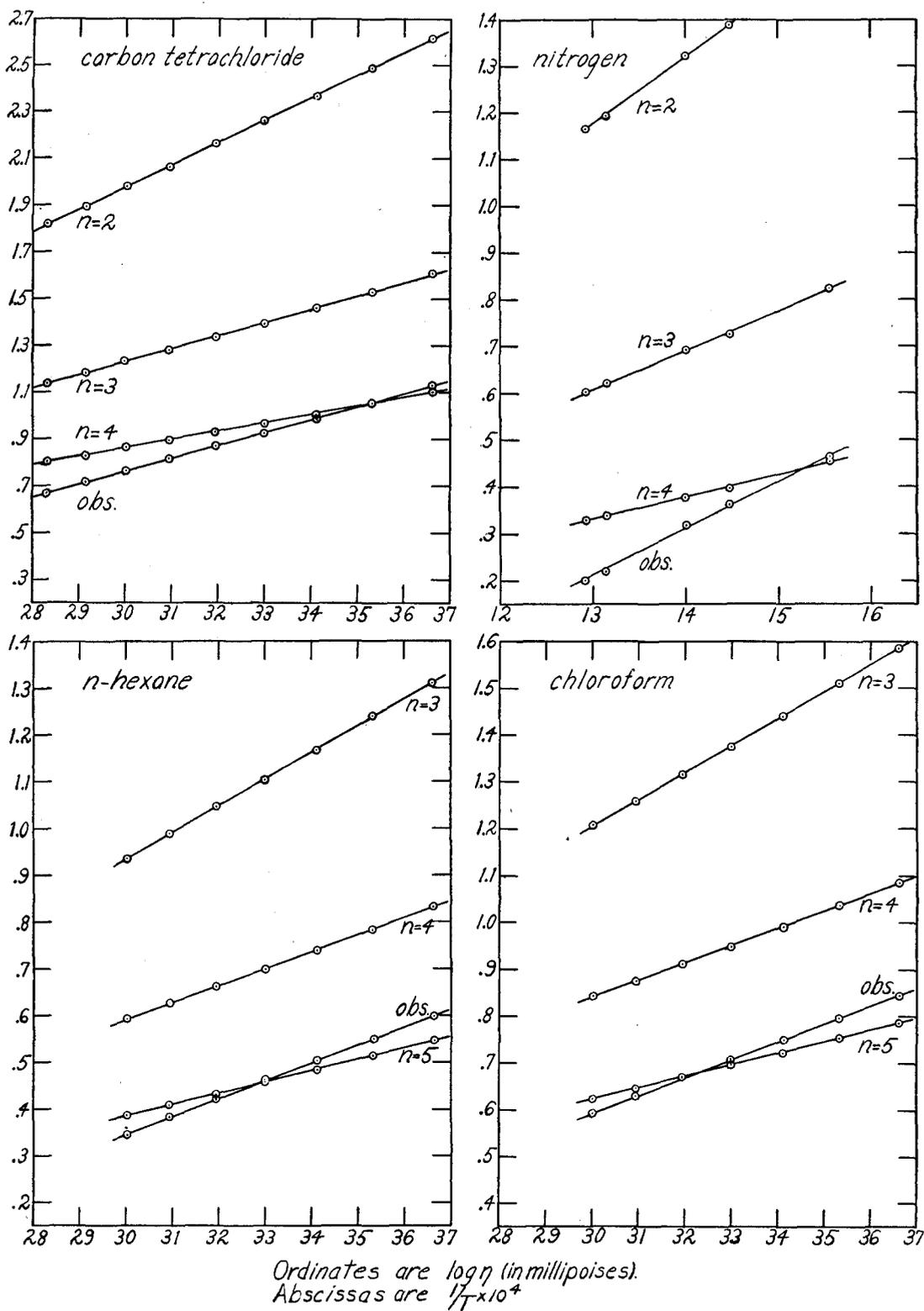


FIG. 1. Plots of $\log \eta$ vs. $1/T$ for observed and calculated viscosities, using integral values of n in Eq. (4).

probable shape of the potential energy surface at kinetic energy levels is considered. There is also considerable evidence that benzene is not the conventional flat hexagon, but that it has approximately a spherical field of force.³ Bernal⁴ has classified cyclohexane as a spherical molecule for reasons which he does not state, and the present result might be considered as confirming the spherical character of cyclohexane. The fact that the activation energy for flow is just one-third the energy of vaporization for these spherical molecules leads to the interesting and useful concept that viscous flow is a sort of vaporization in one degree of freedom.

The other group of liquids with $n=4$, however, are not of spherical symmetry and most of them are polar. For spherical molecules, where all orientations are equivalent, the activation energy of flow is the energy required to make a hole one-third the size of a molecule, i.e., $\Delta E_{\text{vap}}/3$, while for polar or elongated molecules where certain preferred orientations are possible a smaller fraction of the energy of vaporization is sufficient for activation. Naturally if there is a possibility of several orientations the molecule will assume that orientation during flow which requires the least activation energy. That this activation energy should be very close to one-fourth the energy of vaporization for such a wide variety of molecules is an interesting fact.

It will be noted that while the plots with $n=3$ and $n=4$ in Fig. 1 are found to be parallel to the observed, indicating the correct temperature coefficient, the parallel plots do not coincide. Viscosities calculated using Eq. (4) are always

higher than the observed and the antilogarithms of the difference in ordinate of the parallel plots is the factor by which the calculated values are too large. For most liquids the calculated values are too large by a factor of 2 or 3, when the value of n giving the correct temperature coefficient is used. When higher or lower values of n are used, the calculated values are much lower or higher, respectively, as shown in Fig. 1.

This factor of 2 or 3 may be due to several errors in the assumptions we have made. The transmission coefficient, κ , may not be unity, but deviations from unity would make the error even greater. The packing factor, b , may not be 2, but it would not be very different for types of packing other than simple cubic. A quite possible explanation is that a flowing molecule may possess a "persistence of velocity" and when it has once acquired the necessary activation energy it may move more than one intermolecular distance, and λ may be equal to λ_1 , $2\lambda_1$, $3\lambda_1$, etc. for any individual elementary process. It would only be necessary for λ to equal $2\lambda_1$ in 40 percent of the elementary processes to give a calculated viscosity too large by a factor of 2, or in 70 percent of the processes for a factor of 3.

Another possible explanation is that the flow process may be a bimolecular process rather than a unimolecular one, at least in part. According to this mechanism two molecules in adjacent layers, which are moving relative to one another, temporarily form a pair which rotates through an angle of about 90° . The relative motion of successive layers in the liquid is the resultant of many such rotations of pairs of molecules. During the rotation the two molecules will sweep out a volume ΔV , which is the extra volume

³ See Mack, J. Phys. Chem. **41**, 221 (1937).

⁴ Bernal, Trans. Faraday Soc. **33**, 27 (1937).

TABLE II. *Computation of viscosity of CCl₄*

t°C	T°K	V CC/ MOLE	ΔE_{vap} KCAL./ MOLE	$\eta(\text{OBS.})$ MILLI- POISES	n=2		n=3		n=4	
					$\eta(\text{CALC.})$ MILLI- POISES	$\eta(\text{CALC.})/\eta(\text{OBS.})$	$\eta(\text{CALC.})$ MILLI- POISES	$\eta(\text{CALC.})/\eta(\text{OBS.})$	$\eta(\text{CALC.})$ MILLI- POISES	$\eta(\text{CALC.})/\eta(\text{OBS.})$
0	273.1	94.3	7.56	13.47	413	30.7	40.3	2.99	12.7	0.95
10	283.1	95.4	7.43	11.33	305	26.9	33.8	2.98	11.3	1.01
20	293.1	96.6	7.30	9.69	232	24.0	28.8	2.98	10.1	1.04
30	303.1	97.8	7.18	8.42	182	21.6	24.8	2.95	9.2	1.08
40	313.1	99.0	7.06	7.38	145	19.7	21.7	2.94	8.5	1.13
50	323.1	100.3	6.93	6.53	115	17.6	19.1	2.92	7.8	1.19
60	333.1	101.6	6.81	5.84	96	16.4	17.1	2.93	7.3	1.24
70	343.1	103.0	6.68	5.24	78	14.9	15.3	2.92	6.7	1.28
80	353.1	104.4	6.56	4.68	66	14.2	13.8	2.95	6.4	1.36

necessary for the elementary process to take place and would obviously be $V/3$ and $V/4$ of the two classes of molecules. For this bimolecular mechanism, Eq. (1), would be written

$$\eta = \frac{\lambda_1 h}{\kappa \lambda^2 \lambda_2 \lambda_3} \frac{F_n^2}{F_a'^*} \exp \frac{\Delta E_{\text{act}}}{kT},$$

where $F_a'^*$ is the partition function of the bimolecular activated complex, omitting the degree of freedom corresponding to flow. If

$$\frac{F_n^2}{F_a'^*} = \frac{F_n}{F_a^*} = \frac{(2\pi mkT)^{3/2}}{h} V_f^{3/2}$$

the two mechanisms are equivalent, but if

$$\frac{F_n^2}{F_a'^*} < \frac{(2\pi mkT)^{3/2}}{h} V_f^{3/2}$$

the viscosities calculated on the basis of the unimolecular mechanism would be too large.

All these factors might be collected into one parameter in the denominator of Eq. (1)

$$a = b\lambda^2/2\kappa\lambda_1^2$$

if the unimolecular mechanism is retained, or

$$a = (b\lambda^2/2\kappa\lambda_1^2)(F_a'^*/F_n F_a^*)$$

if the bimolecular mechanism is assumed, giving

TABLE III.

LIQUID	ΔE_{vis} CAL./MOLE	ΔE_{vap} AT B.P. CAL./MOLE	$\frac{\Delta E_{\text{vap}}}{\Delta E_{\text{vis}}}$	n
CCl ₄	2500	6600	2.66	3
C ₆ H ₆	2540	6660	2.62	3
Cyclohexane	2890	6700	2.32	3
CH ₄	719	1820	2.53	3
A	516	1420	2.75	3
N ₂	449	1210	2.70	3
CO	466	1310	2.80	3
O ₂	398	1470	3.69	3½
C ₂ H ₄ Cl ₂	2270	6930	3.05	3½
C ₂ H ₄ Br ₂	2590	7890	3.04	3½
Pentane	1580	5510	3.50	4
Hexane	1715	6220	3.61	4
CHCl ₃	1760	6630	3.76	4
C ₂ H ₅ I	1720	6400	3.72	4
C ₂ H ₅ Br	1585	6080	3.84	4
CS ₂	1280	5920	4.63	4
C ₆ H ₅ CH ₃	2120	7240	3.42	4
Ether	1610	5700	3.54	4
Acetone	1655	6400	3.86	4
C ₂ H ₄	793	3500	4.41	4

Eq. (1) with two parameters a and n . The following are the approximate factors by which the calculated viscosities are too high, i.e., values of the parameter a : CCl₄ 3.00, C₆H₆ 3.50, cyclohexane 2.05, CH₄ 3.50, A 2.30, N₂, 2.40, CO 2.50, pentane 1.73, hexane 1.75, heptane 2.00, CS₂ 1.91, ether 2.00, ethyl acetate 2.05, toluene 2.05, acetone 2.20.

Further elucidation of the discrepancy between the observed viscosities and those given by the theory will not be undertaken at this time. The fact that the factors just given are about the same for all liquids and the success of the theory in interpreting the temperature coefficient of viscosity show that the reaction rate theory is essentially correct and that if the elementary process is a bimolecular one it is essentially equivalent to the unimolecular mechanism assumed in the treatment in this paper.

Comparison of n with the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$

In the empirical equation $\eta = Ae^{B/T}$, A is an entropy factor and B is an energy factor. In the flow process as in rate processes generally, energy and entropy of activation tend to compensate each other in such a way as to give the smallest possible free energy of activation. The last section showed that A and B are not constants, but are functions of the temperature (and pressure, too, as will be discussed later), and the nature of the functions was deduced. The fact that A and B appear empirically to be constants over a considerable temperature range is not a coincidence, but is the result of the compensating effect of the energy and entropy of activation making the free energy of activation practically independent of temperature.

If we write $\eta = Ae^{\Delta E_{\text{vis}}/RT}$, ΔE_{vis} will be the experimentally determined quantity $Rd \ln \eta/d(1/T)$. Since this is a constant for normal liquids throughout their normal liquid range, ΔE_{vis} can be considered as an average activation energy of flow in this range. Since ΔE_{vap} varies only slowly with temperature, the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ should be approximately equal to 3 or 4 anywhere in the temperature range where ΔE_{vis} is a constant. Table III gives a comparison of n (as determined in the preceding section) with $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$, where ΔE_{vap} is taken at the normal boiling point for all the liquids in the table.

It is seen that for all the $n=3$ liquids $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ ranges from 2.3 to 2.8, and for all the $n=4$ liquids from 3.4 to 3.9 (except CS_2 and C_2H_4 which are still higher). If the comparison had been made at a lower corresponding temperature, e.g., about four-fifths the absolute boiling

much smaller than the unit of vaporization. The unit of vaporization is the atom, of course, and the unit of flow must then be the much smaller metal ion, i.e., the atom stripped of its valence electron or electrons.

On this hypothesis the activation energy of flow, ΔE_{vis} , would be

TABLE IV.

METAL	MIDDLE OF TEMP. RANGE OF VISCOSITY DATA	ΔE_{vap} KCAL./MOLE	ΔE_{vis} KCAL./MOLE	$\frac{E_{\text{vap}}}{E_{\text{vis}}}$	$\frac{\Delta E_{\text{vap}}}{\Delta E_{\text{vis}}} \left(\frac{r_{\text{ion}}}{r_{\text{atom}}} \right)^3$
Na	500°	23.4	1.45	16.1	2.52
K	480°	19.0	1.13	16.7	3.41
Ag	1400°	60.7	4.82	12.5	3.79
Zn	850°	26.5	3.09	8.6	2.10
Cd	750°	22.5	1.65	13.5	3.96
Hg	250°	13.6	0.65	20.8	2.37
	600°	12.3	0.55	22.2	2.54
Ga	800°	34.1	1.13	30.3	2.53
	600°	15.3	1.44	10.6	4.07
Sn	1000°	14.5	1.70	8.6	3.30
	700°	42.6	2.80	15.9	4.97
Pb	700°	42.6	2.80	15.9	4.97

$$\frac{\Delta E_{\text{vap}}}{3} \times \frac{\text{volume of ion}}{\text{volume of atom}} = \frac{\Delta E_{\text{vap}}}{3} \left(\frac{r_{\text{ion}}}{r_{\text{atom}}} \right)^3$$

or $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}(r_{\text{ion}}/r_{\text{atom}})^3$ should be equal to 3, assuming the metal ions would have spherical symmetry. Table IV shows the experimental values of this latter quantity, using the ionic and atomic radii given by Wyckoff.⁵ The heats of vaporization of metals are not very reliable and are usually not known over a range of temperature. When the temperature variation was known, ΔE_{vap} was taken arbitrarily in the middle of the range over which the viscosities were measured (shown in column 2). In the case of Hg and Sn the average slopes over the two halves of the slightly curved $\log \eta$ vs. $1/T$ plot are given. For the polyvalent metals the following ions were assumed to be the flowing ion: Hg^+ , Sn^{++} , Pb^{++} .

point, all the values of the ratio would have been higher (since ΔE_{vap} would be larger), and the values of the ratio would have clustered around 3 for the $n=3$ liquids and around 4 for the $n=4$ liquids (except C_2H_4 and CS_2). These results show that the value of the experimentally determined ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ at any temperature may be taken as a rough index of the size and shape of the molecule, or more precisely, of the unit of flow. If the value of $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ is much larger than 3 or 4, it indicates that the unit of flow is much smaller than the unit of vaporization (which can be taken as the single molecule in most cases), and if $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ is much smaller than 3 or 4, the reverse is indicated. Examples of both these cases will be discussed below.

While the figures in column 6 are not all equal to 3, they do cluster around 3 and are much closer to 3 than are the figures in column 5, and further, the deviations from 3 are not much greater than the uncertainties in the experimental quantities used in the table. While this

Liquid metals

Most metals give linear $\log \eta$ vs. $1/T$ plots, just as normal covalent liquids do. A few metals, however, notably mercury and tin exhibit a slight curvature. The most striking fact regarding the metals is the large value of the $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ ratio, which ranges from 8 to 25 for different metals as compared to the value of 3 or 4 for normal liquids. This means that the activation energy for flow is much less than $\Delta E_{\text{vap}}/3$ and leads to the conclusion that the unit of flow is

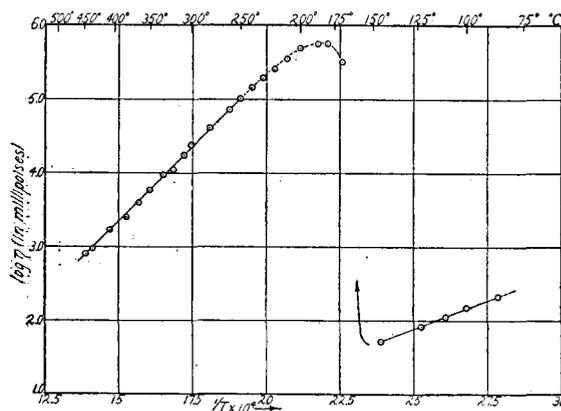


FIG. 2. Plot of $\log \eta$ vs. $1/T$ for liquid sulfur from the data of Rotinjanz.

⁵ Wyckoff, *The Structure of Crystals* (Reinhold Publishing Co., 1931).

result is interesting and suggestive, the hypothesis must not be taken too literally. Since the energy of vaporization of a metal atom is made up of separate work functions of the ion and the electron or electrons, it cannot be so definitely interpreted as the energy necessary to make a hole the size of an atom in the liquid, as in the case of normal covalent liquids. The qualitative concept of the metal ions flowing free of their valence electrons is, of course, quite in harmony with modern ideas on the structure of metals.

Liquid sulfur

As is well known liquid sulfur is a fluid yellow liquid between the melting point and about 160° and also in the supercooled liquid region below the melting point. Above 160° the viscosity increases rapidly, increasing several thousand-fold between 160 and 190°, and thereafter the viscosity decreases in a normal way. The numerous theories advanced to explain these phenomena will not be discussed here. Fig. 2 shows the data of Rotinjanz⁶ plotted $\log \eta$ against $1/T$. Rotinjanz's data show that between 160 and 250° the viscosity of sulfur is a function of the time as well as the temperature, and the values given in that range are only rough averages and probably not equilibrium values.

It is seen that the plot has two linear portions, below 160 and above 250°, for which ΔE_{vis} is 7.04 and 18.35 kcal./mole, respectively. In the region below 160° the molecule is almost certainly a puckered S_8 ⁷ ring, and by comparing this structure with cyclohexane, it seems likely that n would be 3 for this type of molecule. The heats of vaporization of sulfur have been accurately measured by West and Menzies.⁸ Their value of ΔE_{vap} at 120° (the middle of this linear part of the plot) is 2.59 kcal./g atom or 20.7 kcal./mole of S_8 . This is very nearly three times 7.04 the value of ΔE_{vis} in this range, and this may be considered as further evidence toward confirming the S_8 molecule in the liquid in this range.

In the range above 250° the much larger slope of the curve indicates that the molecule is much larger than it is below 160°. This larger sulfur molecule might be either a large ring, a branched

chain or a long straight chain, of which the latter seems most likely to be the correct structure. By analogy with the straight chain hydrocarbons, n should be 4 for this type of molecule, and this would indicate a value of ΔE_{vap} of $4 \times 18.35 = 73.4$ kcal./mole on our hypothesis. West and Menzies give 2.05 kcal./g atom for ΔE_{vap} at 350° (the middle of this linear part of the curve) and comparing this with the value deduced above the molecular weight of the unit of flow is found to be S_{36} . In contrast to this molecular weight of the unit of flow, the unit of vaporization is still S_8 as shown by vapor density data.

This figure of 36 can be interpreted as an average chain length averaged over all the molecules in the liquid and averaged over the whole temperature range from 250 to 450°. At any temperature there is probably an equilibrium mixture of chains of varying length, and as the temperature is raised the average chain length will become smaller as the equilibrium constant changes. The linear relation between $\log \eta$ and $1/T$ is not a sufficient condition for an unchanging molecular state in a liquid. Normal liquids composed of a single molecular species almost without exception give linear $\log \eta$ vs. $1/T$ plots. However, a liquid composed of an equilibrium mixture of several molecular species might also give a linear plot since the equilibrium constant changes according to van't Hoff's equation, which is of the same form of temperature dependence as is the viscosity of a liquid.

The hypothesis had been advanced by Warren and Burwell that the increase in viscosity above 160° is "probably due to the S_8 ring breaking open and forming irregular chains which tangle with one another and give rise to the marked increase in viscosity." Our results give more concrete form to this idea and obviates the necessity of postulating the indefinite concept of tangling of chains since any liquid composed of chains averaging 36 atoms in length, e.g., a hydrocarbon, will be a very viscous liquid.

The normal paraffin hydrocarbons

The values of ΔE_{vis} were determined graphically for the normal paraffins, from pentane to octadecane, using the data mentioned in the list of sources of viscosity data. From pentane to octane the $\log \eta$ vs. $1/T$ plots were straight lines

⁶ Zeits. f. physik. Chemie **62**, 609 (1908).

⁷ Warren and Burwell, J. Chem. Phys. **3**, 6 (1935).

⁸ J. Phys. Chem. **33**, 1880 (1929).

as usual, but for nonane and higher the plots were slightly curved (convex towards the $1/T$ axis), the amount of curvature increasing as the length of the chain increased. Therefore the slope was taken over the temperature range of 20 to 40°, except octadecane where the measurements started at 40°. Best values of the heats of vaporization of these hydrocarbons were furnished by Dr. F. D. Rossini of the National Bureau of Standards in a private communication. The uncertainties in these heats varied from ± 2 percent for C_5H_{12} to ± 6 percent for $C_{18}H_{38}$.

The values of the ratio $\Delta E_{vap}/\Delta E_{vis}$ are given in Table V. The ratio is seen to be about 4 for all these hydrocarbons. This result is surprising and would hardly be possible if these molecules all flowed as extended chain molecules, as a consideration of the mechanism of flow as applied to an extended chain molecule will show. If the hydrocarbon molecules were curled up into a ball shape during the flow process this difficulty would disappear. Such a concept is in harmony with Langmuir's⁹ conclusion that molecules are curled up in this way in the vapor state, since flow can be thought of as vaporization in one degree of freedom. This suggests that the liquid hydrocarbon contains both extended and curled up molecules, and the activated molecules which are responsible for flow, diffusion and vaporization of the liquid are of the curled up type.

Water and other associated liquids

Liquids composed of molecules containing OH or NH groups are those ordinarily called abnormal or associated liquids. Among other anomalies they have much higher viscosities than would be expected from the size and internal

structure of the molecules. For instance, H_2O is much more viscous than H_2S or CH_4 ; C_2H_5OH and $C_2H_5NH_2$ are much more viscous than propane; aniline and phenol are more viscous than toluene; etc. This abnormally large viscosity is, of course, due to the hydrogen bond structure of these liquids. When a molecule in such a liquid flows it must not only break van der Waals and dipole "bonds," but also hydrogen bonds. Table VI shows that $\log \eta$ vs. $1/T$

TABLE VI.

$t^\circ C$	η MILLI- POISES	ΔE_{vis} CAL./MOLE	ΔE_{vap} CAL./MOLE	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$	α ($n=4$)	α ($n=6$)
0	17.95	5060	10,180	2.01	2.24	2.68
50	5.49	3420	9,615	2.81	0.92	1.44
100	2.84	2800	8,980	3.20	0.48	1.04
150	1.84	2110	8,280	3.90	0.04	0.60

is not a straight line for H_2O , but that $\Delta E_{vis}(=Rd \ln \eta/d(1/T))$ decreases rapidly as the temperature increases, and further that the ratio $\Delta E_{vap}/\Delta E_{vis}$ increases with the temperature. Assuming that $n=4$ for water these figures would indicate according to our previous notions that the average unit of flow in water is about two molecules at 0°, and this decreases gradually so that at 150° the average unit of flow is nearly one molecule. A more probable explanation of this behavior is that the single H_2O molecule is the unit of flow at all temperatures, but that when a molecule of water flows the energy of activation for flow is equal to $1/n$ of the energy of vaporization due to undirected attractive forces (van der Waals and dipole attraction) plus *all* of the energy of vaporization due to *directed* forces (hydrogen bonds). Thus if α is the degree of coordination present in water, i.e., the average number of hydrogen bonds attached to a molecule, we have (neglecting repulsive forces):

$$\Delta E_{vap} = \frac{1}{2} [\alpha \epsilon_{H-bond} + \sum_{i=2}^N \epsilon_i \text{ (van der Waals)} + \sum_{i=2}^N \epsilon_i \text{ (dipole)}]$$

and

$$\Delta E_{vis} = \frac{1}{2} \alpha \epsilon_{H-bond} + 1/n (\Delta E_{vap} - \frac{1}{2} \alpha \epsilon_{H-bond}). \quad (5)$$

TABLE V.

HYDROCARBON	RANGE	ΔE_{vis} KCAL./MOLE	ΔE_{vap} AT 25° KCAL./MOLE	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$ AT 25°
$n-C_5H_{12}$	0°-b.p.	1.58	5.71	3.61
$n-C_6H_{14}$	0°-b.p.	1.73	6.96	4.01
$n-C_7H_{16}$	0°-b.p.	1.91	8.11	4.25
$n-C_8H_{18}$	0°-b.p.	2.14	9.21	4.30
$n-C_9H_{20}$	0°-40°	2.44	10.21	4.20
$n-C_{10}H_{22}$	0°-30°	2.60	11.11	4.28
$n-C_{11}H_{24}$	0°-30°	3.06	11.96	3.91
$n-C_{14}H_{30}$	20°-40°	3.60	14.21	3.95
$n-C_{16}H_{34}$	20°-40°	4.01	15.51	3.87
$n-C_{18}H_{38}$	40°-60°	4.15	16.76	4.03

⁹ Colloid Symposium Monograph 3, 54 (1925).

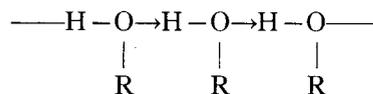
Then the rapid decrease of η and ΔE_{vis} with rising temperature is due to the decrease in the number of hydrogen bonds that have to be broken for flow to take place. This activation energy due to hydrogen bonds can be called structure activation energy of flow, and it will be an important factor in any liquid or mixture of liquids containing OH or NH groups. This structure activation energy is the cause of the very high viscosities of glycol, glycerol, sugars, etc., since a three-dimensional network of hydrogen bonds can be formed in these liquids. Lacking hydrogen bonds glycol and glycerol would be expected to have about the same viscosity as butane and 3-methyl pentane, respectively.

If n is assumed to be equal to 4 for water by analogy with other polar liquids (see Table I), and the energy of the hydrogen bond is assumed to be 3000 cal./mole,¹⁰ Eq. (5) can be used to compute the degree of coordination in liquid water at different temperatures. The results are given in column 6 of Table VI. These values of α are undoubtedly low, for n would probably be larger than 4 for water. In an open structure such as water has, a smaller fraction of the energy of vaporization (considering only that portion due to undirected forces) should be sufficient to activate the flow process than in ordinary closer packed liquids. If n is taken as 6, for example, the values of α in column 7 result. This calculation is, of course, very approximate, but it does show the decrease in the degree of coordination with rising temperature. Burnham, Cross and Leighton¹⁰ concluded from Raman spectra that in the range 25 to 90° water is slightly more than two coordinated, which is in approximate agreement with the value of α at lower temperatures in Table VI. It seems likely, however, that α should decrease significantly between 25 and 90°, although possibly not as much as indicated in Table VI.

Similar considerations can be applied to other associated liquids, the maximum possible coordination being twice the number of OH or NH groups in the molecule. Monohydric alcohols would have a maximum coordination of two, and the fact that ethyl alcohol and water have about

¹⁰ Burnham, Cross and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

the same viscosity indicates that ethyl alcohol must possess a large fraction of its maximum two-coordination. Alcohols may be composed of chains



with the R groups arranged roughly parallel in the liquid, or possibly rings containing three or four molecules linked in a similar fashion. Glycol has a maximum coordination of four, the same as water, and the fact that glycol is 20 times as viscous as water indicates that the degree of coordination is much higher in glycol than in water. This is probably due to the fact that the two OH groups are separated in glycol giving less interference between the hydrogen bonds attached to the two groups. Similarly glycerol has a maximum coordination of six, so that as little as half of the maximum coordination will permit a three-dimensional network of hydrogen bonds, giving rise to the very high viscosity of glycerol. Conclusions such as these in this paragraph are necessarily very approximate since the relative contributions to the energy of vaporization of van der Waals, dipole and hydrogen bond forces, and especially of repulsive forces, are not known for any associated liquid. Further work is in progress in an attempt to throw light on this question utilizing viscosity data.

The variation of viscosity with pressure

We have the general relationship that the energy to make a hole the size of a molecule at any pressure is the energy required to take a molecule from the liquid to vacuum. At small pressures the latter energy is the usual energy of vaporization as used in the preceding treatment. The general expression for the energy of making a hole the size of a molecule is however

$$v(p_{int} + p_{ext}),$$

i.e., the work of expanding a volume v against the combined internal and external pressure, where v is the volume occupied by a molecule at p_{ext} , i.e., V/N . At small pressures $Vp_{int} = \Delta E_{vap}$ and Vp_{ext} is negligible compared to ΔE_{vap} . At high pressures, however, Eq. (4) must be written in the more general form:

$$\eta = 1.090 \cdot 10^{-3} \frac{M^{1/2} T^{1/2}}{V^{5/3} (p_{\text{int}} + p_{\text{ext}})} e^{V(p_{\text{int}} + p_{\text{ext}})/nRT}, \quad (6)$$

where b has again been taken as 2, and n will have the same value for both temperature and pressure variation, at least, for moderate pressures (up to several thousand atmospheres).

If the internal pressure, $p_{\text{int}} = (\partial E / \partial V)_T$, can be evaluated, Eq. (6) can be used to calculate the variation of viscosity with pressure. Or conversely, the experimental values of the variation of viscosity with pressure can be used to calculate the internal pressures, which can then be compared with those derived from other sources. This has been done for several liquids using Bridgman's viscosity-pressure data¹¹ and compressibility data.¹² The internal pressure at one atmosphere was taken as $\Delta E_{\text{vap}}/V$, and the internal pressures at higher pressures were obtained by trial and error in order to get the experimentally observed relative viscosities (relative to the viscosity at atmospheric pressure). The results for ether and *n*-pentane (using $n=4$) are shown in the circles of Fig. 3. Also shown are values of the internal pressures calculated from the thermodynamic equation

$$p_{\text{int}} = (\partial E / \partial V)_T = T(\partial p / \partial T)_V - p. \quad (7)$$

The squares are the internal pressures calculated in this way by Hildebrand¹³ from Bridgman's earlier compressibility data on ether. The triangles are the internal pressures calculated for ether and *n*-pentane in the same way from Bridgman's later data.

The internal pressures calculated from the viscosity data lie on a much smoother curve than those calculated from compressibilities, and from the nature of the agreement it is hard to say which is likely to be the most nearly correct set of values. For several other liquids, $\text{C}_2\text{H}_5\text{Br}$, $\text{C}_2\text{H}_5\text{I}$, CS_2 , all using Bridgman's earlier compressibility data, the agreement was not quite as good, the internal pressures from viscosities being higher than those from compressibilities, particularly at high pressures. In the curves in Fig. 3 the same tendency is also noted at high pressures. If the internal pressures calculated from compressi-

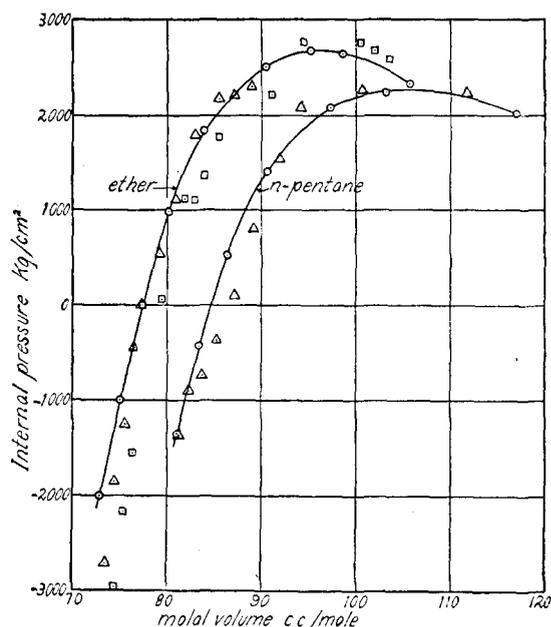


FIG. 3. Plots of internal pressure vs. molal volume for ether and *n*-pentane. The circles are values computed from Eq. (6) using Bridgman's data for viscosity under pressure. The triangles and squares are values computed from Eq. (7) using Bridgman's newer (1931) and older (1914) compressibility data, respectively.

bilities are assumed to be the true ones, this would mean that a little larger fraction of the volume occupied by a molecule is necessary for the elementary process to occur at high pressures where the molecules have been squeezed in closer together. Or in other words, a little higher activation energy is required than that to be expected from the simple picture. When short range forces, such as exchange and dipole forces, come into play, the potential energy ceases to be a function of volume alone and depends on relative orientation. This is exemplified in marked degree in water as discussed in the last section. In such liquids the activation energy for flow depends not only on the fact that a hole is required before the elementary process can take place, but also on the directed bonds to neighbors, since directed bonds to neighbors cannot be made in the relatively disordered activated state. Even normal liquids will at sufficiently high pressures show the same directed potentials arising from exchange interaction, and this may be the cause of the activation energy of flow at high pressures being higher than that given by the simple theory.

¹¹ Proc. Am. Acad. Arts Sci. **61**, 57 (1926).

¹² Ibid. **49**, 1 (1913-14); **66**, 185 (1931).

¹³ Phys. Rev. **34**, 984 (1929).

TABLE VII. Approximate calculation of viscosity of as a function of pressure using Eq. (6) and assuming $p_{int} = \Delta E_{vap}/V$.

p KG/CM ²	ETHYL BROMIDE		ETHYL ETHER		CARBON DISULFIDE	
	(η/η_0) calc.	(η/η_0) obs.	(η/η_0) calc.	(η/η_0) obs.	(η/η_0) calc.	(η/η_0) obs.
1	1.00	1.00	1.00	1.00	1.00	1.00
500	1.29	1.32	1.42	1.55	1.22	1.23
1000	1.63	1.67	1.95	2.11	1.49	1.45
2000	2.62	2.44	3.74	3.27	2.20	2.03

The liquids which have $n=3$, CCl_4 , C_6H_6 and cyclohexane, have such low freezing pressures that the viscosities and compressibilities have not been measured above 1500 kg/cm², and this range is insufficient to make a significant test with these liquids.

The calculated internal pressures, $(\partial E/\partial V)_T$, are the slopes of the potential energy-volume curve of the liquid, and they suffice to construct the general features of the potential energy curve. The point where the internal pressure is a maximum, i.e., where

$$\left(\frac{\partial p_{int}}{\partial V}\right)_T = \left(\frac{\partial^2 E}{\partial V^2}\right) = 0,$$

is the inflection point of the potential energy curve where the repulsive forces are just beginning to become effective. The point where the internal pressure is zero, i.e., $p_{int} = (\partial E/\partial V)_T = 0$, is the minimum of the potential energy curve. At smaller volumes $(\partial E/\partial V)_T$ becomes a larger and larger negative quantity, corresponding to the rapidly increasing repulsive energy.

The pressure range from atmospheric pressure up to about 2000 kg/cm² includes the broad maximum part of the internal pressure-volume curve, and so in this range of pressures the energy of vaporization measured at atmospheric pressure can be taken as approximately equal to Vp_{int} , and the viscosity as a function of pressure can be computed approximately up to about 2000 kg/cm² using Eq. (6) without requiring any compressibility data, except that required to know the volumes at the particular temperature in question. Table VII shows the results of some calculations at 30°. At pressures higher than 2000 kg/cm² this computation is increasingly poor as the true internal pressure deviates more and more from $\Delta E_{vap}/V$.

The Molecular Volumes and Expansivities of Liquid Normal Hydrogen and Parahydrogen

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The molecular volumes at saturation of liquid normal hydrogen and parahydrogen between 14° and 20.4°K were measured with a fused quartz dilatometer, the amount of hydrogen being determined from the pressure of the gas in a calibrated flask at a measured temperature. The results are represented by the equations:

$$V(n\text{-H}_2) \text{ cm}^3 \text{ mole}^{-1} = 24.747 - 0.08005T + 0.012716T^2,$$

$$V(p\text{-H}_2) \text{ cm}^3 \text{ mole}^{-1} = 24.902 - 0.0888T + 0.013104T^2.$$

At the normal boiling point of $n\text{-H}_2$ (20.38°K), $V(n\text{-H}_2) = 28.397 \pm 0.010$ and $\Delta V(p-n) = 0.138 \pm 0.010$. The expansivity of $p\text{-H}_2$ is only slightly greater than that of $n\text{-H}_2$. The change observed in the molecular volumes of H_2 in passing from the state in which the molecules rotate ($o\text{-H}_2$) to the state in which they do not rotate ($p\text{-H}_2$) is

opposite in direction to the change observed in other substances when passing between these two states of molecular rotation and nonrotation. The changes in "lattice" energies are also of opposite sign. It is shown that the random state of orientation of the axes of $p\text{-H}_2$ molecules makes the state of nonrotating $p\text{-H}_2$ fundamentally like that of rotation in other substances at high temperatures. The differences in the molecular volumes and "lattice" energies of the condensed phases of $o\text{-H}_2$ and $p\text{-H}_2$ arise from a difference in the magnitude and symmetry of the intermolecular forces of repulsion. These differences in the forces of repulsion result from a difference in the distributions of the average electron density of $o\text{-H}_2$ and $p\text{-H}_2$ molecules arising from the difference in the rotational motion of the two varieties at low temperatures.