Properties of the Liquid State
II: Description of Viscosity Over the Entire Liquid Range*)

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With 5 tables

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It has been shown in the preceding paper (1) that the structure of a generalized liquid may be regarded as consisting of domains of inactive molecules clustered together and separated from one another by regions occupied by active molecules having energies in excess of a characteristic threshold value, $E_a$. The number of molecules, $a$, occupying an edge of such an inactive domain is, on the average, given by

$$a = n \frac{(1 - e^{-E_a/RT})^{1/3}}{1 - (1 - e^{-E_a/RT})^{1/3}}.$$  \[1\]

From this model, the dynamic viscosity can be represented in terms of the size of inactive domains by

$$\eta = \frac{q}{V^{1/3}} e^a.$$  \[2\]

where $V$ is the mean molecular volume of the liquid. Combination of Eqns. [1] and [2] yields the following general expression for the variation of viscosity with temperature:

$$\ln \eta = n \frac{(1 - e^{-E_a/RT})^{1/3}}{1 - (1 - e^{-E_a/RT})^{1/3}} + \ln q - \ln V - \frac{3}{3}.$$  \[3\]

In this relationship, the viscosity coefficient is a function of the molecular volume

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and two other parameters, consisting of the threshold energy, $E_a$, which is considered to be characteristic of the liquid state, and a characteristic constant, $q$, which is specific to the property being studied. In practice, all experience shows that the variation of molar volume with changing temperature in a liquid is relatively small. Therefore, without great loss of accuracy, one may consider the cube root of that quantity to be nearly constant (as a first approximation), thereby defining the pseudo-constant,

$$Q = q^{1/3}.$$  \[4\]

whence the viscosity coefficient may be expressed as

$$\log \eta = n \frac{(1 - e^{-E_a/RT})^{1/3}}{2.303 [1 - (1 - e^{-E_a/RT})^{1/3}]} + \log Q.$$  \[5\]

In the application of eqn. [5] to actual data, it is therefore necessary to evaluate $E_a$ and $Q$ for the substance in question. In principle, only two experimental points, $\eta_1$ at $T_1$ and $\eta_2$ at $T_2$, are required for this purpose. In practice, it is found that best results are obtained if one of these points is near the normal boiling temperature and the other is not more than about 50 °C above the freezing point. With two such points, one may apply eqn. [5] twice to eliminate
the "constant", \( Q \): 

\[
\frac{1}{n} \log \frac{\eta}{\eta_i} = \frac{(1 - e^{-E_a/RT})^{1/3}}{2.303 \left[ 1 - (1 - e^{-E_a/RT})^{1/3} \right]} - \frac{(1 - e^{-E_a/RT})^{1/3}}{2.303 \left[ 1 - (1 - e^{-E_a/RT})^{1/3} \right]}. \tag{6}
\]

In determining the value of the constant, \( n \), which is the number of molecules in the thickness of an activated zone between two adjacent inactive domains, there is at present no quantitative means to compute it. However, we shall assume that it is unity (i.e., that the zone is of monomolecular thickness) and shall later present a qualitative argument to show that this assignment is reasonable.

An analytical solution of eqn. [6] to determine \( E_a \) (on the basis of the foregoing assumption) is impractical, so that a numerical method must be used. Since eqn. [6] is quite general and does not depend on any special substance or conditions, one may construct a table of its values. Noting that 

\[
\log \left( \frac{\eta}{\eta_i} \right) = \frac{1}{2.303} (a - a_i). \tag{6a}
\]

Table 1 gives the values of \( a/2.303 \) as determined by eqn. [1].

In the use of table 1, it is noticed that 

\[
\frac{E_a/RT}{E_a/RT} = \frac{T_1}{T_2} = \theta. \tag{7}
\]

so that for the trial and error determination of the correct value of \( E_a/RT \) (designated hereinafter by \( x \)) one first computes the relationship of \( T_1/T_2 = \theta \) corresponding to an experimental value of the two viscosity coefficients that lead to \( \log (\eta/\eta_i) \). For \( a/2.303 \) a value is found from the table, using a trial value for \( x \), and the associated value of \( a_i = \theta x \) is similarly introduced into the table to obtain a value of \( a/2.303 \). The difference between these two values should yield the experimental quantity, \( \log (\eta/\eta_i) \), according to eqn. [6a]. If the computed quantity exceeds the experimental one, the \( x \)-value assumed in the next trial is chosen smaller than before, and vice-versa. A series of approximations performed in this manner finally yields agreement between the computed and the experimental viscosity functions, from which the corresponding \( x \)-value then permits one to establish the energy, \( E_a \).

As soon as \( E_a \) is known, one may apply eqn. [5] to determine the characteristic parameter, \( Q \). In table 2, we present the two parameters, \( E_a \) and \( \log Q \), which have been determined in this way for twenty paraffin hydrocarbons. Table 3 gives the same parameters for a number of associated liquids.

When \( E_a \) and \( Q \) have been found in this manner for a liquid, employing two widely separated experimental points for the purpose, it is then possible to introduce their numerical values into eqn. [5] and calculate the viscosity of the liquid at any temperature within the normal range. The precisions with which such calculations reproduce the experimental viscosities are also listed in tables 2 and 3, respectively, together with the temperature range involved in each case. It will be seen that the agreement between the computed and observed viscosities is rather good. The largest disagreements for

### Table 1

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<th>( E_a/RT )</th>
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<th>( 0.01 )</th>
<th>( 0.02 )</th>
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