ON THE THEORY OF LIQUIDS.

Part VI. The Rate of Reactions in Liquids.

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In a series of papers the author has developed a modification of Edser's theory of liquids and deduced a number of equations relating various properties of liquids, one to another. In this modified theory, each molecule of a liquid, particularly near the melting-point, is regarded as vibrating within an associated spherical space of diameter σ, which it keeps clear from other molecules by virtue of its thermal motion. The vibrations take place under forces of attraction and repulsion between the molecules. In addition to this oscillatory motion, a small fraction of the molecules undergo diffusion, but near the melting-point the translatory motions are small and can be neglected. The spherical spaces are regarded as closely packed so that σT is related to VT the molecular volume by the equation,

\[ N\sigma_T^3 = VT \sqrt[3]{2} \]  

where \( N \) is the number of molecules in 1 g.-mol.

This theory leads directly to the constancy of the parachor for the surface tension of a liquid has been shown to be given by the equation,

\[ \gamma = \frac{\pi \mu}{4 (m - 5) \sigma^{m+1}} \]  

where \( \mu \) and \( m \) are respectively the coefficient and index of the attractive force between the molecules. (2) combined with (1) gives

\[ \gamma = \frac{\pi \mu}{4 (m - 5)} \frac{N^{3}}{V^{3}} \frac{m+1}{m+1} \]  

\[ \gamma = \frac{\pi \mu}{4 (m - 5)} \frac{N^{3}}{V^{3}} \frac{m+1}{m+1} \frac{m-1}{2} \]  

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2 Part V, loc. cit., p. 467.
where \( P \) is a constant. If \( m \) is put equal to 11, (4) becomes
\[
\gamma = \frac{P^4}{V^4} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)
\]
where \( P \) is the parachor constant.

Bradley\(^3\) independently put forward a similar view of the structure of a liquid, and has formulated a theory of unimolecular reactions in the liquid phase, in which it is assumed that reaction of a solute molecule occurs as a result of a collision with a solvent molecule bounding its spherical space, provided that the collision involves energy exceeding the critical energy, \( E \). In this paper Bradley’s views are incorporated with the frequency equation developed by the author, in his previous papers, and are shown to lead to results which agree moderately well with the experimental observations on a number of unimolecular reactions. A theory of bimolecular reactions in solution differing from that of Bradley is also developed and applied to calculate experimental results.

Unimolecular reactions.—It has been shown\(^4\) that the vibration frequency in its spherical space of a molecule of a liquid with a normal parachor is given by
\[
\nu = \frac{8 \sqrt{6} P^4}{7 \sqrt{\pi} V^4} \frac{\sigma}{\sqrt{mkT}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6)
\]
where \( k \) is Boltzmann’s constant, and \( m \) is the mass of a liquid molecule. Combining (1) and (6) and inserting the numerical values of the constants we have,
\[
\nu^* = 1.40 \times 10^{12} \frac{P^4}{V^{11/3} M^4 T^4} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)
\]
where \( M \) is the molecular weight of the solute. The number of collisions per second of \( n \) molecules with the surrounding molecules is accordingly
\[
k = 2.8 \times 10^{12} \frac{P^4}{V^{11/3} M^4 T^4} \frac{-E}{e^{RT}} (\frac{E}{RT})^{\gamma-1} \frac{1}{|f-1|} \quad \ldots \quad \ldots \quad (8)
\]
it being assumed that \( E \) is defined by \( 2f \) squared terms.

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\(^3\) J., 1934, 1910.

\(^4\) Part V, loc. cit., p. 471.

* It is assumed that the frequency of the solute molecule is the same for the solute in solution as for the solute in the liquid state.
From (8) we have

\[
\frac{d \ln k}{d (1/T)} = -\frac{E}{R} + \frac{11T^2a}{3} + (f - \frac{1}{2})T \quad \ldots \quad \ldots \quad (9)
\]

where \(a\) is the thermal coefficient of cubical expansion,

\[
= -\frac{E_A}{R} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (10)
\]

where \(E_A\) is the Arrhenius critical increment.

Hence

\[
E_A = E - \frac{22T^2a}{3} - (2f - 1)T \quad \ldots \quad \ldots \quad \ldots \quad (11)
\]

(8) can be transformed into

\[
E \left( \frac{E}{RT} \right)^{f-1} \frac{1}{|f-1|} = 3.57 \times 10^{-12} \frac{\sqrt{11\beta}}{T^6} \frac{1}{F^4} \quad \ldots \quad \ldots \quad (12)
\]

from which if \(k\) and \(f\) be known, \(E\) can be calculated and inserted into (11) to give \(E_A\), which can be compared with the experimental result.

\(k\) is, of course, known from experiment; for \(f\) integral values ranging from 1 upward are tried to determine if a relatively small value (say <5) will enable a satisfactory value of \(E_A\) to be calculated.

It will be seen from Table I that with one exception the observed values of \(E_A\) can be satisfactorily reproduced, using values of \(f\) which do not in any instance exceed 4. The agreement is as good as that obtained by Moelwyn-Hughes\(^5\) by the application of his collision theory; for most of the reactions given in Table I he postulates values of \(f\) (his \(F = f - 1\)) greater by 2 than are required by the present theory.

For those reactions in Table I for which \(f\) takes the value 1, it may be supposed that the two squared terms involved are to be referred to the kinetic and oscillation potential energies of the decomposing molecule; the energy of the solvent molecule is here not effective in producing decomposition.

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TABLE I.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$P_\dagger$</th>
<th>$M$</th>
<th>$T$</th>
<th>$V_\dagger$</th>
<th>$\alpha \times 10^4$</th>
<th>$k^*$ (obs. sec.$^{-1}$)</th>
<th>$E_A$* (obs.)</th>
<th>$E_A$ (calc.) $^{(11, 12)}$</th>
<th>$f$</th>
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† Where data are not available, values for compounds of a similar type or similar molecular weight have been employed; approximate values are sufficient for the purposes of calculation.


The experimental values of $E_A$ are accurate in most instances to within about ± 500 cals.
Bimolecular reactions.—We assume as before that the vibratory motions only, of the molecules need be considered. Reaction occurs when a solute molecule of type 1 collides with sufficient energy, with one of type 2 which bounds its spherical space. If \( n_1, n_2 \) and \( n_s \) denote respectively, the number of solute molecules of type 1 and 2, and of molecules of the solvent in 1 c.c., then the number of collisions which the \( n_1 \) molecules of type 1 make with the boundaries of their spherical spaces is \( 2n_1v_1 \) per sec. The number of these collisions which involve molecules of type 2 is
\[
Z_{12} = 2n_1v_1 \frac{n_2}{n_s + n_1 + n_2} = \frac{2n_1n_2v_1}{n_s} \quad \ldots \quad \ldots \quad \ldots \quad (13)
\]
since \( n_s \) is large compared with \( n_1 \) and \( n_2 \).

Similarly, the number of collisions per sec. of \( n_2 \) molecules of type 2 with molecules of type 1 is given by
\[
Z_{21} = \frac{2n_1n_2v_2}{n_s} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (14)
\]

\( Z_{12} \) and \( Z_{21} \) should be identical, but are not so, because in each calculation the frequency of one type of molecule only has been considered. We may, however, as an approximation use the mean of the frequencies and put
\[
Z_{12} = Z_{21} = \frac{n_1n_2}{n_s} (v_1 + v_2) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (15)
\]
The number of fruitful collisions per sec. with critical energies greater than \( E \) will then be
\[
\frac{n_1n_2}{n_s} (v_1 + v_2) e^{\frac{-E}{RT}} \left( \frac{E}{RT} \right)^{\frac{f-1}{f-1}} \frac{1}{f-1}.
\]
Hence the rate of chemical change becomes
\[
\frac{dn}{dt} = \frac{n_1n_2}{n_s} (v_1 + v_2) e^{\frac{-E}{RT}} \left( \frac{E}{RT} \right)^{\frac{f-1}{f-1}} \frac{1}{f-1} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (16)
\]
The bimolecular velocity constant expressed in litres per g.-mol. per sec. is given by
\[
k = \frac{1}{n_1n_2} \frac{dn}{dt} \frac{N}{1000} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (17)
\]
so that we have
\[
k = \frac{N}{1000} \frac{v_1 + v_2}{n_s} e^{\frac{-E}{RT}} \left( \frac{E}{RT} \right)^{\frac{f-1}{f-1}} \frac{1}{f-1} \quad \ldots \quad \ldots \quad \ldots \quad (18)
\]
Inserting the values of \( v_1 \) and \( v_2 \) [see (7)] and putting \( n_z = \frac{N}{V_z} \), we have

\[
k = \frac{(1.40 \times 10^9)}{T^1} V_z \left( \frac{P_1^4}{V_1^{11/3} M_1^{4/3}} + \frac{P_2^4}{V_2^{11/3} M_2^{4/3}} \right) \frac{-E}{RT} \left( \frac{E}{RT} \right)^{r-1} \frac{1}{|f-1|} \quad (19)
\]

and

\[
\frac{-E}{e^{RT}} \left( \frac{E}{RT} \right)^{r-1} \frac{1}{|f-1|} = \frac{(7.14 \times 10^{-10})}{T^1} \left[ \frac{P_1^4}{V_1^{11/3} M_1^{4/3}} + \frac{P_2^4}{V_2^{11/3} M_2^{4/3}} \right]^{-1} \quad (20)
\]

To differentiate \( k \) we write (19) in the following approximate form,

\[
k = \frac{(1.40 \times 10^9)}{T^1} V_z \frac{2P^4}{M^{4/3}T^1} \frac{-E}{RT} \left( \frac{E}{RT} \right)^{r-1} \frac{1}{|f-1|} \quad (21)
\]

where \( P^4, V^{11/3} \) and \( M^{4/3} \) are the averages of respectively, \( P_1^4 P_2^4, V_1^{11/3} V_2^{11/3}, \) and \( M_1^{4/3} M_2^{4/3} \). Differentiating (21) we obtain,

\[
d \ln k \over d(1/T) = - \frac{E_A}{R} = - \frac{E}{R} - T^2 a_x + \frac{11}{3} T^2 a + \frac{T}{2} (2f - 1) \quad (22)
\]

\[
= - \frac{E}{R} + \frac{8}{3} T^2 a_x + \frac{T}{2} (2f - 1) \quad (23)
\]

since \( a \) may be put equal to \( a_x \) without serious error. We now proceed as before to calculate \( E \) from (20) and hence \( E_A \) from (23) using small integral values of \( f \).

Bradley\(^6\) has pointed out that suitable examples of bimolecular reactions between unionised molecules are rare, but that no serious difficulty is introduced, if one of the reactants is an unionised molecule, and the ions considered are not strongly solvated. It will be seen from Table II that for a variety of such reactions, the experimental value of \( E_A \) can be reproduced with values of \( f \) equal to 1 or 2 indicating that the critical energy of collision for bimolecular reactions involves few internal degrees of freedom.

It would appear, therefore, that the theory of the structure of liquids, which has been developed by the author, is capable of affording a satisfactory picture of the mechanism of simple unimolecular and bimolecular reactions in solution.

\(^6\) Loc. cit., p. 1916.
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