Relation Between Fluidity, Temperature and Chemical Constitution of Pure Liquids

By E. C. Bingham and S. D. Stookey

In a recent report[1] on the results of a general survey of the field of viscosity, the fact is made evident that there is so far apparently no simple equation expressing accurately a direct relationship between viscosity of liquids and temperature. With regard to the form of equations evidently considered best by the investigating committee, the statement is made (1): "As to the influence of temperature, it has been found that the characteristic decrease of the viscosity of a liquid with rising temperature can, with a fair amount of approximation, be described by the exponential formula $\eta = A e^{B/RT}$."

Also, the committee makes the following statement (1): "In the homologous series of the aliphatic hydrocarbons, alcohols, fatty acids, etc., an increase of the viscosity generally seems to take place with the number of CH_2— groups of the chains, although even a merely rough proportionality or other regularity appears to be out of the question."

We believe that the equation to be discussed in this paper expresses, in a simple and accurate form, a definite relationship between temperature and viscosity; and that in addition it affords a "well defined regularity" in the viscosity–temperature functions of successive members of a homologous series of liquids.

The equation is

$$\varphi/T = a + bT + \ldots \tag{1}$$

where φ denotes the fluidity in rhes (reciprocal poise) and T is temperature in degrees absolute.

It will be shown that for liquids whose molecules are not longer than nine or ten carbon atoms, equation (1) expresses the fluidity–temperature relationship very accurately without introducing higher terms.

Also, equation (1) shows a very definite and striking relationship between the fluidity–temperature functions of successive members of a homologous series, which will be discussed in section II. This relationship follows from the fact that the constant a in equation (1) is a function of the homologous series to which the compound belongs, and b a function of the molecular weights of the members of the series; so that an equation may be obtained containing constants which are functions only of the series concerned, and not of individual members of the series.

The modified equation is

$$\varphi/T = A_a + \alpha T 10^{(\beta/M - \gamma/M^2)} \tag{2}$$

M denoting molecular weight, and α, β and γ being constants.

Equation (2) has been found to be almost as accurate as the simple one, equation (1), and so makes it possible to calculate quite precisely the fluidity of any member of the series (as high in the series as the two-constant form of equation (1) is valid), at any temperature at which the substance is in the liquid state, by the use of only four constants.

This paper will be divided into three sections: section I dealing with the application of equation (1) to individual compounds; section II, with the application of equation (2) to homologous series, and section III, with the anomalous behavior of the aliphatic acids, aliphatic alcohols, and water.

Section I: Application of Equation (1)

Procedure.—The best available viscosity data were used. The data consisted of the absolute viscosities measured at small temperature intervals from 0° to the boiling point of each liquid studied, or to 100°. An attempt was made to choose representative members of as many classes of liquids as possible for which reliable data could be obtained, so that each liquid for which data are given in Table I is typical of several to which the equation may be applied with accuracy. The major part of the viscosity measurements were made by Thorpe and Rodger.[2]

Values of the constants a and b in equation (1) were determined by the method of least squares. The fluidities were then calculated at various temperatures from these constants, and the deviation from the observed fluidities recorded.

Table I gives the values of the constants for a number of compounds, with the standard, or root

(1) Second Report on Viscosity and Plasticity, prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam, 1938, pp. 37, 57–58.

(2) F. Thorpe and J. Rodger, J. Phil. Trans., London, **185A**, Part II, 397 (1894).

mean square, percentage deviation (% S. D.) of the calculated fluidity from the observed, for each compound.

TABLE I

CONSTANTS a AND b OF EQUATION (1) WITH % STANDARD DEVIATION

All viscosity measurements by Thorpe and Rodger.[2]

Substance	$-a$	b	% S. D.
Hexane	1.0773	0.007311	0.2
Isohexane	1.1315	.007741	.2
Hexine	1.16315	.0082135	.1
Heptyl bromide	0.68091	.003225	.15
Propyl iodide	.5797	.003555	.2
Chloroform	.5989	.004105	.0
Carbon tetrachloride	.8431	.0040765	.3
Ethyl ether	1.1231	.008791	.0
Acetone	0.9133	.006727	.1
Methyl propyl ketone	.9521	.005566	.2
Ethyl sulfide	.8765	.005605	.2
Amyl mercaptan	.8276	.004620	.3
Secondary amyl mercaptan	.8764	.005115	.3
Acetaldehyde	.9317	.008423	.1
Acetic anhydride	.8382	.004146	.1
Ethyl acetate	1.1072	.006368	.1
Bromine	0.3710	.002433	.2
Nitrogen tetroxide	.9018	.005852	.1
Benzene	1.2535	.006070	.0
Toluene	0.9331	.005165	.15

Av. 0.15

Discussion of Results.—Table I demonstrates that equation (1) is valid for a large number of classes of pure liquids, including straight and branched chain saturated aliphatic hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, alkyl bromides and iodides, ethers, aldehydes,

ketones, anhydrides, esters, thioalcohols (normal and secondary), alkyl sulfides, and inorganic liquids, including elements and liquefied gases. The average root mean square deviation of the calculated fluidities from those observed is 0.15% for all the liquids in Table I.

This list does not exhaust the range of applicability of equation (1). The only class of liquids for which it is known to be invalid is the alcohols, which will be discussed in Section III.

Section II: Application of Equation 2

Procedure.—Upon examination of the constants a and b, it became evident that a is practically identical for all members of a non-associated homologous series (as high in the series as equation (1), without introduction of higher terms, is valid). That is, when the ratio φ/T is plotted against the absolute temperature, the straight lines representing the members of the series all converge at the absolute zero of temperature.

Also, it was found that the values of the constant b of equation (1) are an exponential function of the molecular weight within a given series, conforming to the equation

$$b = \alpha 10^{\beta/M - \gamma/M^2} \qquad (3)$$

M being the molecular weight, and α, β and γ constants.

These facts make it possible to express the fluidity–temperature relations of all the members of a series (within the above-stated limits) by means of equation (2) given above.
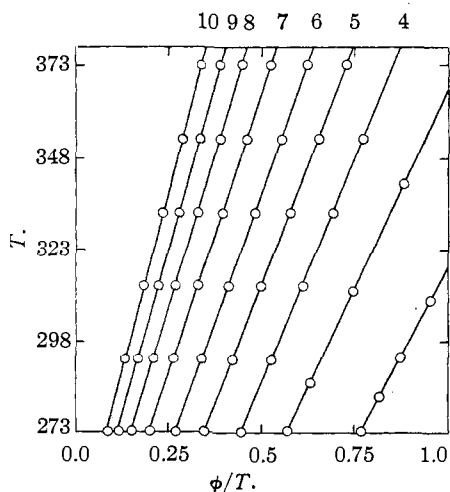

Fig. 1.—Alkyl bromides: φ, fluidity in rhes; T, °K. The numerals denote the number of carbon atoms in the compound.
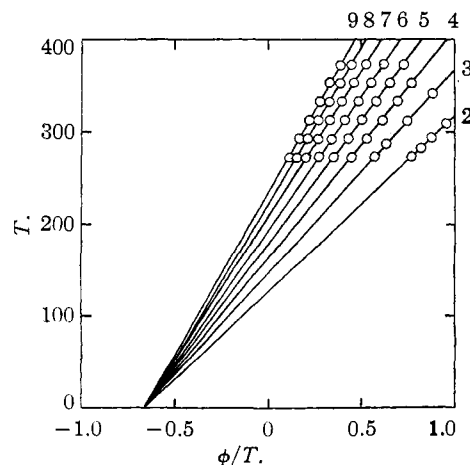

Fig. 2.—Alkyl bromides: curves of Fig. 1 extrapolated to 0°K., showing convergence at absolute zero of the straight lines representing series members.

TABLE II

Alkyl bromides: $\varphi/T = -0.6655 + 0.001252\ T\ 10^{(80.08/M - 1357.6/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Ethyl bromide (2)	0.6425	0.005158	0.005238	0.0	0.2	0.4
Propyl bromide (2)	.6880	.004600	.004525	.0	.3	1.6
Butyl bromide (3)	.6255	.003940	.004065	.8	.9	0.9
Amyl bromide (3)	.6921	.003804	.003721	.2	.7	1.6
Hexyl bromide (3)	.6985	.003540	.003437	.3	.9	1.9
Heptyl bromide (3)	.6809	.003225	.003177	.2	.6	0.8
Octyl bromide (3)	.6655	.002980	.002982	.7	.7	0.8
Nonyl bromide (3)	.6311	.002727	.002834	.8	.8	3.5

Alkyl iodides: $\varphi/T = -0.5339 + 0.000162\ T\ 10^{(346.97M - 20759/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Methyl iodide (2)	0.50595	0.004112	0.004208	0.1	0.2	0.2
Ethyl iodide (2)	.5160	.003755	.003818	.1	.3	.3
Propyl iodide (2)	.5797	.003555	.003410	.2	.7	.7

Aliphatic n-hydrocarbons: $\varphi/T = -1.0533 + 0.002040\ T\ 10^{(61.97/M - 1229.5/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Pentane (2)	1.0708	0.008660	0.008600	0.2	0.2	0.8
Hexane (2)	1.0773	.007311	.007233	.25	.3	1.7
Heptane (2)	1.0894	.006542	.006430	.4	.4	1.1
Octane (2)	1.0581	.005769	.005754	.4	.4	0.9
Nonane (4)	1.0357	.005170	.005225	.3	.6	0.5
Decane (4)	0.98855	.004634	.004837	.8	2.1	2.2

Aliphatic isohydrocarbons: $\varphi/T = -1.1392 + 0.003630\ T\ 10^{(25.76/M - 145.22/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Isopentane (2)	1.1850	0.009259	0.009100	0.1	0.2	0.2
Isohexane (2)	1.1315	.007741	.007767	.2	.2	.2
Isoheptane (2)	1.1012	.006826	.006945	.4	.9	.9

n-Mercaptans: $\varphi/T = -0.8014 + 0.001578\ T\ 10^{(63.49/M - 1636.1/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Propyl mercaptan (4)	0.8506	0.005778	0.005607	0.0	0.3	0.6
Butyl mercaptan (4)	.8550	.005226	.0050535	.6	.9	1.4
Amyl mercaptan (4)	.8276	.004620	.004538	.3	.7	0.7
Hexyl mercaptan (4)	.8157	.004193	.004149	.3	.5	0.6
Heptyl mercaptan (4)	.7746	.003747	.003831	.5	.6	1.1
Octyl mercaptan (4)	.7617	.003459	.003584	.8	1.8	2.1
Nonyl mercaptan (4)	.7249	.003168	.003408	.7	4.2	5.9

Secondary mercaptans: $\varphi/T = -0.8405 + 0.001361\ T\ 10^{(85.54/M - 2790.3/M^2)}$

Substance	$-a$	b	b'	% S. D. (a, b)	% S. D. (A_s, b')	% S. D. $(A_s, \alpha, \beta, \gamma)$
Propyl mercaptan (4)	1.0997	0.0068355	0.005956	0.1	1.5	1.6
Amyl mercaptan (4)	0.8764	.005115	.004996	.3	0.5	0.7
Hexyl mercaptan (4)	.8781	.004652	.0045345	.4	.9	1.4
Heptyl mercaptan (4)	.8456	.004178	.004161	.6	.7	1.3
Octyl mercaptan (4)	.8167	.003798	.003873	.2	.7	0.8
Nonyl mercaptan (4)	.7856	.003468	.003640	.7	2.3	3.8

The individual values of the constant a were averaged to obtain the series constants "A_s" for each of six aliphatic series: normal hydrocarbons, isohydrocarbons, normal bromides, normal iodides, normal mercaptans, and secondary mercaptans.

The values of b were recalculated from the new series constants, and the fluidities redetermined.

Finally, the constants α, β and γ in equations (2) and (3) were calculated, and the fluidities redetermined with all restrictions, according to equation (2).

Figures 1 and 2 are graphs, φ/T vs. T, for a typical series, the alkyl bromides. In Fig. 1, successive lines represent successive members of

(3) A. R. Bayer, Master's Thesis, Lafayette College, 1933.

(4) E. C. Bingham and H. J. Fornwalt, J. Rheol., 1, 372 (1930).

the series, from ethyl bromide on the right to decyl bromide on the left. The numbers of the lines denote the number of carbon atoms. Figure 2 is identical with Fig. 1 except that the lines are extrapolated to absolute zero and decyl bromide is not represented.

In Table II, a and b are the constants of equation (1); b' is the new value of b calculated from the series constant A_s; and the equations contain all the series constants A_s, $-\alpha$, β and γ of equation (2). The last three columns of Table II contain the percentage standard deviation, or root mean square deviation (denoted by % S. D.) of the calculated fluidities from the observed. The first of the three columns represents the deviation of fluidity calculated from a and b; the second, that calculated from A_s and b'; and the last column, that calculated when equation (2), with all the series constants, is applied.

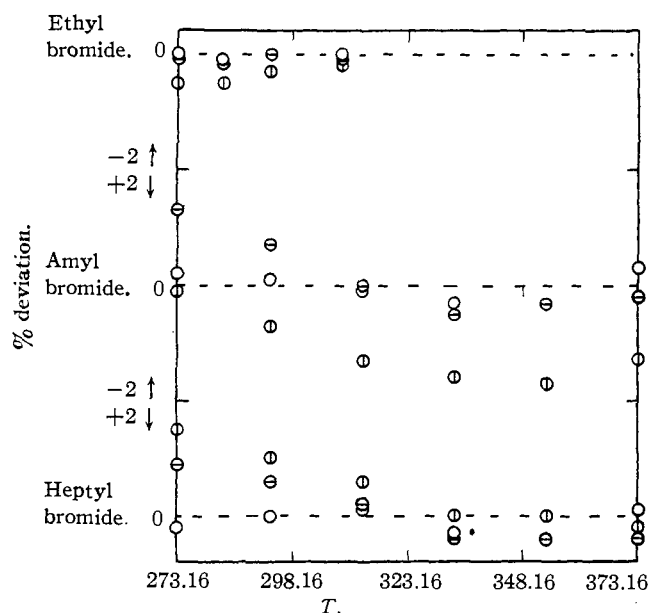Figure 3 is a deviation chart, % deviation in fluidity vs. temperature for some representative aliphatic bromides.

TABLE IIIA
ALIPHATIC ACIDS (2)

Acid	$-a$	b	% S. D.
Formic	0.90435	0.003737	1.4
Acetic	.8632	.003885	0.45
Propionic	.7224	.003522	.2
Butyric	.7637	.003489	.8

TABLE IIIB
WATER (5)

Temp. range, °C.	$-a$	b	% S. D.
0–25	1.6439	0.0067635	0.3
25–100	1.9149	.007675	

Max. dev. 0.5

TABLE IV
FLUIDITY OF ALKYL BROMIDES (3)

Bromide	Fluidity in rhes at given temperature, °C.					
	0.0	20.0	40.0	60.0	80.0	100.0
Butyl	122.0	154.4	192.3	230.8	271.8	321.2
Amyl	94.6	123.9	156.4	192.3	230.6	270.6
Hexyl	73.4	99.1	128.4	161.0	195.5	231.5
Heptyl	54.7	77.5	102.9	131.4	161.8	194.9
Octyl	41.4	61.2	84.0	108.9	136.7	166.5
Nonyl	31.7	48.9	69.2	92.3	117.4	144.5
Decyl	24.3	39.3	75.2	77.7	100.8	125.4

Fig. 3.—Deviation chart. Representative plot of the percentages of deviation of calculated fluidity from observed: open circles represent φ calculated by equation 1; circles with horizontal diameters, φ calculated from a_s (series constant) and b'; circles with vertical diameters, φ calculated by equation 2, with all series constants.

The fluidities of the higher members of the alkyl bromide series have been determined by Bayer[3] and are given at the end of this paper in Table IV.

Discussion of Results.—The average standard deviation of the calculated fluidity from the observed, when equation (3) is applied to individual members of the series, is 0.4% for eight alkyl bromides, 0.1% for three alkyl iodides, 0.4% for six n-hydrocarbons, 0.2% for three isohydrocarbons, 0.45% for seven n-mercaptans, and 0.4% for six secondary mercaptans. The equation fits the data for higher members of the series than those given here with almost equal accuracy, but the percentage deviation increases gradually with increasing molecular weight, due, presumably, not to the increased weight of the molecules (since bromine obeys the equation) but to the effect of the long chains. The curvature is in a direction which shows that for longer molecules the fluidity increases more rapidly at higher temperatures than at low temperatures. Addition of a term of the power series in T of equation (1) corrects for this tendency, if desired.

When the individual values of a are averaged to give a series value A_s, the average standard deviation for bromides is 0.6%, iodides 0.4%, n-hydrocarbons 0.7%, isohydrocarbons 0.4%, n-mercaptans 1.3%, secondary mercaptans 0.8%.

Applying all restrictions, according to equation

(2), the average standard deviation for n-bromides is 1.4%, n-iodides 0.4%, n-hydrocarbons 1.2%, isohydrocarbons 0.4%, n-mercaptans 1.8%, secondary mercaptans 1.1%.

Section III: Anomalous Liquids

Procedure.—The only marked abnormalities noted thus far in the behavior of liquids with regard to equations (1) and (2) occur in compounds which contain a hydroxyl radical. The three abnormal types of liquids are the aliphatic acids, alcohols, and water. Each of the three exhibits a different sort of anomaly.

Table IIIA contains the values of a and b (equation 1) for the first four members of the aliphatic acid series, and the percentage standard deviations. Figure 4 shows the corresponding curves, φ/T vs. T, the curves being numbered according to the number of carbon atoms in the compound represented.
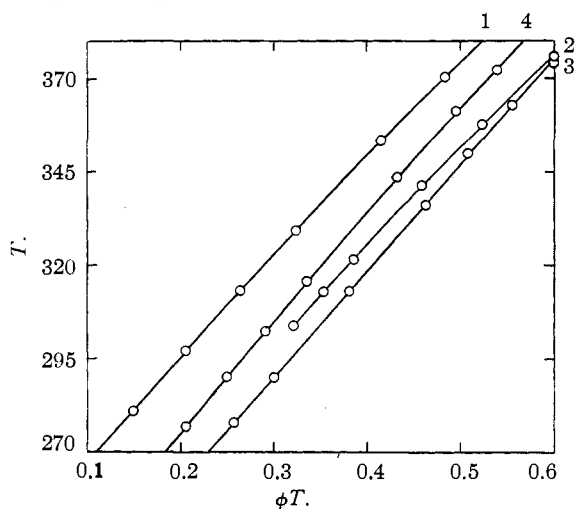

Fig. 4.—Aliphatic acids: the numerals denote the number of carbon atoms in the acids represented: formic, acetic, propionic and butyric. Note contrast between relative positions of curves as compared to Fig. 1.

Table IIIB gives the constants a and b for water; Fig. 5 shows the curve φ/T vs. T. The data used are an average of the observations of six observers.[5]

Discussion of Results.—The results show that the aliphatic acids obey equation (1) quite well, the average standard deviation being only 0.7%. In nearly every case, however, there is a definite though slight tendency toward curvature.

(5) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 339.

On the other hand, comparison of Fig. 4 with Fig. 1 makes very evident the contrast between the apparently random variation of the slopes and positions of the curves for acids, and the regular variation for a typical non-associated series.

The fact that the acids obey equation (1) may be explained by considering that they form nearly stable compounds in their association; for which there is evidence from X-ray measurements.[6]

The slight curvature then is probably caused by the slight instability of the associated liquids.

The φ/T vs. T curves of the alcohols all show very decided curvature. This may possibly be caused by the fact that the alcohols, although associated, form unstable compounds, and that the degree of association varies with temperature.

The φ/T vs. T curve for water (Fig. 5) is a straight line from 0 to 25°, and from 25 to 100°, curving slightly in the neighborhood of 25°. We have, therefore, applied equation (1) twice, and the two equations reproduce the observed fluidity with a standard deviation of 0.3%, the maximum deviation being 0.5%.
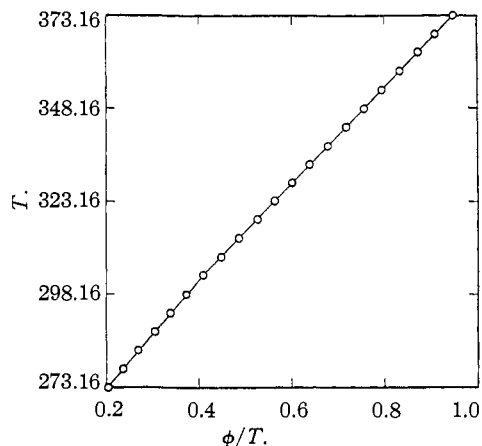

Fig. 5.—Water.

Summary

A simple equation relating fluidity directly to temperature has been shown to fit the data very accurately for a large number of liquids, apparently failing only for alcohols. The equation also shows a definite relation between the viscosity–temperature functions of successive members of a homologous series, making it possible to calculate the viscosity of any member of a non-associated series up to ten carbon atoms at any temperature by means of only four constants.

The fluidities of the aliphatic bromides from

(6) Müller, J. Chem. Soc., **123**, 2054 (1923).

butyl bromide to decyl bromide between 0 and 100° as determined by Bayer, are given.

Note: Equation (1) has been found to apply to some types of solutions as accurately as to pure

liquids. Further investigations are being made along this line.

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The Mechanism of Solvolytic Reactions of Organic Halides and the Use of Activity Coefficients in the Equation for a Reaction Velocity

BY PAUL D. BARTLETT

Of the theories about the dependence of reaction velocity in solution upon the solvent, the two which have received the most attention in this century are those of van't Hoff[1] and of Brönsted,[2] later refined by other workers and commonly known, respectively, as the "activity-rate theory" and the "transition-state theory." It is consistent with both theories to regard the activated complex as a molecular species in equilibrium with the reactants. The activity-rate theory then demands that the rate of reaction shall be proportional to the fugacity of the activated complex, while the transition-state theory makes the rate proportional to the concentration of this complex.

For reactants forming nearly ideal solutions below their limits of solubility, the activity-rate theory predicts specific reaction rates inversely proportional to their solubilities in a series of solvents. This prediction was shown by von Halban[3] in 1913 to fall hopelessly short of the facts in the formation of p-nitrobenzyltrimethylammonium chloride. Here the introduction of corrections for solubility increased the range of observed velocity constants in eighteen solvents from 9300-fold to over 400,000-fold, when according to the theory it should have rendered the corrected rate independent of solvent.

It has thus long been evident that the activity-rate theory does not possess general validity. Since this is so, the success recently attained by Olson and Halford[4] in reviving this theory and applying it to the calculation of reaction rates in a graded series of methanol–water and ethanol–water mixtures is surprising. The rate of production of hydrogen chloride by t-butyl chloride in these series of solvents varies 100-fold for the

former and 750-fold for the latter series, and these rates have been calculated in terms of the vapor pressures of the reactants within less than the uncertainty of the data employed in the calculation.

Such agreement cannot be entirely accidental, and from the standpoint of the theory of reaction velocity it is important to try to decide between two possibilities. Either (1) the activity-rate theory is fundamentally true for a solvolytic reaction in mixed solvents, while lacking general validity, or (2) it is not fundamentally true, but represents a useful approximation because of special relationships among the quantities appearing in the equations. It is the purpose of this paper to approach this question by inquiring whether the activity-rate theory fits the data of Olson and Halford uniquely, and to draw such conclusions as may be possible about the factors determining the rate of reaction and the mechanism of this particular reaction.

The liberation of hydrogen chloride from t-butyl chloride in these experiments proceeds with the formation of three organic products—t-butyl alcohol, methyl t-butyl ether, and isobutylene. The reaction is an unfortunate one for testing a kinetic formulation on account of the difficulty in making a convincing demonstration of what is going on. The reaction has been variously designated by Farinacci and Hammett[5] as polymolecular, by Olson and Halford[4] as bimolecular, and by Ingold, Hughes,[6] and their co-workers as unimolecular, depending upon the extent to which attention has been focussed upon the role of the solvent in the rate-determining step. In a recent note[7] the British workers have indicated that the difference between their "unimolecular" and Hammett's "polymolecular" is a matter of language

(1) Van't Hoff, *Vorlesungen*, 1, 219 (1901).

(2) Brönsted, *Chem. Rev.*, **5**, 269 (1938); also *Z. physik. Chem.*, **115**, 327 (1925).

(3) Von Halban, *ibid.*, **84**, 129 (1913).

(4) Olson and Halford, THIS JOURNAL, **59**, 2644 (1937).

(5) Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).

(6) Bateman, Hughes and Ingold, *J. Chem. Soc.*, 881 (1938).

(7) Bateman, Hughes and Ingold, THIS JOURNAL, **60**, 3080 (1938).