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"Structure" in Liquids and the Relation between the Parameters of the Arrhenius Equation for Reactions in the Condensed Phase¹

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On the basis of the liquid state being quasi-crystalline, a modification of the transition state theory leads to a simple equation for the temperature dependence of the fluidity, which involves a characteristic frequency of molecular vibration. The parameters of the fluidity equation are shown to have a linear correlation for certain liquids. The quasi-crystalline picture is then extended to a simple collision theory of uni- and bimolecular reactions in solution, and it is shown that the known correlation of the parameters of the Arrhenius equation arises from the fluidity correlation.

I. INTRODUCTION

IN recent years, increasing emphasis has been placed on the concept of "structure" in the liquid state. This train of thought was initiated by the discovery of the x-ray diffraction of liquids by Debye and Scherrer and in the hands of Debye,⁴ Zernike, Prins⁵ and others, this concept has received its mathematical formulation. Eyring and his co-workers⁶ and Lennard-Jones and Devonshire⁷ have extended it to predict and explain many properties of the liquid state.

It is the purpose of the present paper to utilize such a model of the liquid state to explain certain phenomena connected with the kinetics of simple non-ionic reactions* in solution. To do this it is necessary first to discuss the effect of the structural concept in relation to the viscosity (or better, "fluidity") of liquids.

¹ Presented in a preliminary form before the Division of Physical and Inorganic Chemistry of the American Chemical Society, 103rd Meeting, Memphis, Tennessee, April 20-24, 1942. Publication delayed by military service.

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³ This paper is from the thesis submitted by Mr. Paul Becher to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1942.

⁴ P. Debye, *Physik. Zeits.* **31**, 348 (1930).

⁵ F. Zernike and J. A. Prins, *Zeits. f. Physik.* **41**, 184 (1927); J. A. Prins, *ibid.* **56**, 617 (1929); *Naturwiss.* **19**, 435 (1931).

⁶ H. Eyring, *J. Chem. Phys.* **4**, 283 (1936); J. F. Kincaid and H. Eyring, *ibid.* **6**, 620 (1938); R. H. Ewell and H. Eyring, *ibid.* **5**, 726 (1937). Also, S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

⁷ J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. A* **163**, 53 (1937); **165**, 1 (1938).

* By a "simple non-ionic reaction" is meant one in which (all things being equal) the rate of reaction is independent of the dielectric properties of the solvent.

II. THE FLUIDITY OF LIQUIDS

Imagine that there exists in the liquid a quasi-crystalline lattice, exhibiting short range order. The lattice is, to be sure, imperfect, but it is these very imperfections which can be considered to be characteristic of the liquid state. Further imagine that, in this quasi-crystalline lattice, the molecules are vibrating with characteristic frequencies, which, for the sake of simplicity, will be assumed to be harmonic and all the same for a given liquid.

Now, because of the imperfections of the lattice, next to any given molecule there may exist a vacant lattice-site. While the molecule is vibrating with a small amplitude, a translation to this neighboring site is not possible, but if the amplitude of vibration should increase (increased energy), then, at a certain critical amplitude the vibration goes over into a translation, and the molecule occupies the next lattice site. The energy required for this jump is (harmonic vibration),

$$\epsilon = 2\pi^2 m \nu^2 q_c^2, \quad (1)$$

where m is the mass of the molecule, ν is the characteristic frequency, and q_c is the critical amplitude.

In the absence of any external shear, there will, of course, be an equal likelihood that this shift in lattice position will take place in all possible directions of the quasi-lattice. However, when a shearing force is applied, there will be an excess of jumps in the direction of shear, and flow occurs. Since, for Newtonian liquids at least, the shearing force will not affect the energy require-

ments for such a lattice jump, the energy of Eq. (1) is evidently the activation energy for flow, and may now be designated ϵ_ϕ , or per mole, E_ϕ .

The foregoing considerations can now be given a more precise mathematical form. In terms of the transition state theory, Eyring⁶ has indicated that the fluidity of a Newtonian liquid may be given by

$$\phi = (V/hN) \cdot (F^\ddagger/F) \exp(-E_\phi/RT), \quad (2)$$

where ϕ is the fluidity, V the molar volume, F^\ddagger and F , the partition functions of the activated and unactivated molecules, respectively, and E_ϕ , the activation energy of flow, which may be considered to have the form of (1). N , h , R , and T have the usual meanings.

Now, Eyring has considered that F^\ddagger and F differ only in the *translational* portions of the partition function, and is thus led to an expression for the fluidity which involves a free volume per molecule, which then has to be calculated—a not too simple problem. However, from the considerations indicated above it would appear more likely that they differ in the *vibrational* partition functions. If this is taken to be the case, Eq. (2) will take the form

$$\begin{aligned} \phi &= V\nu/NkT \exp(-E_\phi/RT) \\ &= V\nu/RT \exp(-E_\phi/RT), \end{aligned} \quad (3)$$

where, of course, E_ϕ is defined in terms of Eq. (1).^{**}

As yet nothing has been said about the nature of the vibrational frequency alluded to in Eqs. (1) and (3), except to describe it as the frequency with which the molecule executes harmonic vibrations about its equilibrium position in the quasi-crystalline lattice. It is desired to give an absolute value to this frequency. It may, in fact, be readily calculated by an extension of our picture of the liquid state.

Debye's⁸ modification of the Einstein⁹ specific heat theory of crystalline substances supposes that the $3N$ vibrations of the N particles which make up the lattice are the first $3N$ overtones of a

continuous solid with the same elastic constants as the crystal. Hence, the $3N$ th frequency is given by

$$\nu_D = C(3N/4\pi V)^{1/3}, \quad (4)$$

where C is of the nature of an average velocity of sound in the medium (average because of the possibility of transverse as well as longitudinal waves), and V is the volume. For our purposes, we may assume that all the particles have the same frequency, given by Eq. (4). This is not unjustified; the most probable frequency of a real crystal has nearly that value.

Thus ν_D , as defined by Eq. (4), is identified with the vibrational frequency of the molecules in the quasi-crystalline lattice. One simplification results in the application to the liquid state; since a liquid will not support transverse vibrations, C is no longer an average velocity of sound in the medium, but is equal to the experimentally measured value of the velocity of sound in the liquid. This enables one to calculate the frequency of vibration of the molecule if the velocity of propagation of sound in the liquid, and the molar volume are known.

We now have the value of every parameter in Eq. (3) except q_c , the critical amplitude. In principle, it should be possible to estimate this parameter from a knowledge of the molecular volume and from a knowledge of the x-ray diffraction pattern of the liquid. In practice, however, because of the asymmetry of the molecules, the problem is a fairly complex one. Since the assumption of harmonic motion has introduced an element of uncertainty in any case, it is perhaps futile to attempt this calculation, which would, at best, still be an estimate.

The equation, however, may be tested quite critically in another way. Since we can determine experimentally values for E_ϕ , the activation energy of flow, we may assume a reasonable value for q_c and calculate the frequency from Eq. (1), that is

$$\nu_E = (E_\phi/2\pi^2mq_c^2N)^{1/2} \quad (5)$$

(where we have written the frequency with the subscript E to indicate the manner of calculation). If our choice of q_c has been correct, then ν_E should equal ν_D . Now, it is very reasonable to assume that q_c will be about the same for most substances, hence if the same choice of q_c gives

^{**} It is perhaps significant to point out that Eyring does not totally disregard the possibility that the different partition function is the vibrational one; this possibility is mentioned in the first paper listed in reference (6).

⁸ P. P. Debye, Ann. d. Physik **39**, 789 (1912).

⁹ A. Einstein, Ann. d. Physik (4), **22**, 180 (1907).

good agreement between ν_E and ν_D for a number of substances, we may feel that the theory has been rather critically tested.

In Tables I and II the results of such a calculation are set forth. For alcohols, a value of 0.75A has been used; this could be approximately a hydrogen bond radius. For other types of liquids a value of 0.50A appears to be of the correct order of magnitude. The agreement between ν_E and ν_D is seen to be quite good, certainly better than the usual "order of magnitude." Thus, it should be readily possible to calculate the energy of activation of flow for most liquids to within less than 15 percent, using a value of about 0.50A for the critical amplitude of vibration and the experimentally determined velocity of sound in the liquid.

It is of interest to note that Simha,¹⁰ proceeding on a somewhat different concept of the flow process, has derived a similar expression for the temperature dependence of the fluidity, differing only in the inclusion of a packing factor.

III. RELATION OF THE PARAMETERS FOR FLUIDITY

The form of Eq. (3) may be experimentally verified in a rather interesting manner. A discussion of the significance of this result will be deferred, however, until later in the paper.

Equation (3) may be written

$$\phi = B \exp(-E_\phi/RT),$$

in which form it is the familiar semi-empirical equation suggested by Arrhenius¹¹ and de Guzman.¹²

Comparison of the above equation with Eq. (1) shows that

$$B = f(\nu)$$

and

$$E_\phi = F(\nu^2),$$

from whence it would appear that, for a series of liquids, a relationship should exist between B and E_ϕ . A plot of $\log B$ vs. E_ϕ does, indeed, yield a straight line for various groups of liquids—a functional relationship which has not previously

been demonstrated. It should be noted, however, that the actual *form* of the relationship is not an immediate consequence of the equations given, even assuming the relative constancy of q_c . While to this extent the relation is somewhat accidental, this is unimportant; it is that the relation does in fact exist that is significant.

In Fig. 1 this relation is demonstrated for a number of alcohols, while in Fig. 2 it is shown to exist for aliphatic acids. From its partially accidental nature, this relationship does not necessarily have to be restricted to members of a homologous series, as is shown in Figs. 3 and 4, the latter showing *two* such correlations. It should be noted that iodobenzene and nitrobenzene do not fit these correlations.***

It has been demonstrated that the temperature dependence of fluidity of a mixture of simple liquids can be accurately represented by Eq. (3). Consequently, we felt it reasonable to assume that in the case of a binary mixture, the effective frequency reflected in the energy of fluidity through Eq. (3) would be of the nature of an "average" frequency. Thus, it would vary slightly with concentration, and we should expect to find a similar correlation existing between various concentrations of binary mixtures. This is shown in Figs. 5–7 for the systems benzene-ethanol, water-acetone, and water-ethanol, respectively. The existence of this correlation has also been verified for many more mixtures over a large range of $\log B$ and E_ϕ values, but space considerations forbid their representation here.

By extension, this correlation should also hold for ternary systems, and that this is indeed the case is shown in Fig. 8 for the system water-acetone-ethanol.

IV. REACTIONS IN A QUASI-CRYSTALLINE SOLVENT

A. Unimolecular Reactions

Let us now consider the rates of unimolecular reactions in solution from the point of view of the solvent as quasi-crystalline.

Consider a dilute solution of a molecules of reactant A in b molecules of an inert solvent B , $b \gg a$. Since the solution is dilute, each mole-

*** The reasons for the choice of these particular liquids will appear presently.

¹⁰ R. Simha, J. Chem. Phys. 7, 302 (1939).

¹¹ S. Arrhenius, Meddel. Vetenskapsakad. Nobelinst. 3, 20 (1916).

¹² J. de Guzman, Anal. Soc. Espan. Fis. Quim. 11, 353 (1913).

cule of A is effectively isolated and will be surrounded by a crystal coordination sphere of n solvent molecules B ($6 \leq n \leq 12$). Assume that the position of each molecule A relative to the equilibrium positions of the solvent molecules is fixed; then any collisions which take place will occur as a result of the lattice vibrations of B . Further, one may assume that collisions may only take place when the vibrational energy of the B molecules is such that the amplitude of vibration is *very nearly* that which would cause the molecule to tear itself from its lattice point (Eq. (1)). These molecules will then possess an energy which is a definite fraction of the activation energy of flow, i.e., $E_\phi' = \sigma E_\phi$, $0 < \sigma \leq 1$. In general, one may take $\sigma \approx 1$ ($E_\phi' \approx E_\phi$).

Now of the n molecules surrounding each molecule A , only $n \exp(-E_\phi'/RT)$ will, therefore, have sufficient energy to collide with the reactant molecule at the extreme of its vibration, and since the molecule is vibrating with a frequency ν , there will be $n\nu \exp(-E_\phi'/RT)$ such collisions per second for each A molecule. Thus the total number of collisions taking place between solvent and reactant molecules per second will be

$$Z_{AB} = an\nu \exp(-E_\phi'/RT), \quad (6)$$

where Z_{AB} is clearly the collision number for the solution.

From the theory of unimolecular reactions¹³ it is immediately clear that only those collisions in which more than a certain critical energy (the activation energy) is distributed among a specified number of internal degrees of freedom contribute to the reaction. Thus, the number of collisions *leading to reaction* per second is

$$\begin{aligned} Z_{AB} \frac{1}{(S-1)!} \left(\frac{E_a}{RT} \right)^{S-1} \exp\left(-\frac{E_a}{RT}\right) \\ = \frac{an\nu}{(S-1)!} \exp\left(-\frac{E_\phi'}{RT}\right) \exp\left(-\frac{E_a}{RT}\right) \\ = \frac{an\nu}{(S-1)!} \exp(-E_{\text{obs}}/RT) \end{aligned} \quad (7)$$

¹³ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, England, 1939), Chapter XII, especially pp. 519-530.

TABLE I. Calculated vibrational frequencies in alcohols. $q_c = 0.75A$

| Compound | ν_D (Velocity of sound) $\times 10^{-13}$ | ν_E (Fluidity) $\times 10^{-13}$ |
|----------|--|---|
| Methanol | 0.173 | 0.172 |
| Ethanol | 0.164 | 0.168 |
| Propanol | 0.155 | 0.166 |
| Butanol | 0.152 | 0.152 |
| Pentanol | 0.149 | 0.151 |

where $E_{\text{obs}} = E_\phi' + E_a$ is the observed activation energy, and where E_a is the activation energy which the reaction would require if it were carried out in the gas phase, with all solvent effects removed. The observed change in activation energy for the same reaction from solvent to solvent is thus explained as the effect of the contribution from E_ϕ' .

Equation (7) therefore represents the number of A molecules which react per second.

Now, by definition, for a unimolecular reaction of the first order

$$-d(A)/dt = k_1(A), \quad (8)$$

where (A) is the concentration of A in moles per liter. Now, it may readily be shown that

$$(A) = 10^3 a / b V_B, \quad (9)$$

where V_B is the molar volume of the solvent.

Substituting Eq. (9) in (8), we obtain

$$-da/dt = k_1 a. \quad (10)$$

It is evident that the left-hand side of Eq. (10) represents the number of molecules reacting per

TABLE II. Calculated vibrational frequencies in various liquids. $q_c = 0.50A$

| Compound | ν_D (Velocity of sound) $\times 10^{-13}$ | ν_E (Fluidity) $\times 10^{-13}$ |
|----------------------|--|---|
| Chloroform | 0.106 | 0.111 |
| Ether | 0.113 | 0.133 |
| Chlorobenzene | 0.148 | 0.125 |
| Nitrobenzene | 0.169 | 0.142 |
| Benzene | 0.155 | 0.165 |
| Aniline | 0.196 | 0.218 |
| Toluene | 0.117 | 0.137 |
| Ethylbenzene | 0.143 | 0.130 |
| Acetone | 0.150 | 0.104 |
| Carbon tetrachloride | 0.105 | 0.113 |
| n-Hexane | 0.115 | 0.128 |
| n-Heptane | 0.115 | 0.126 |

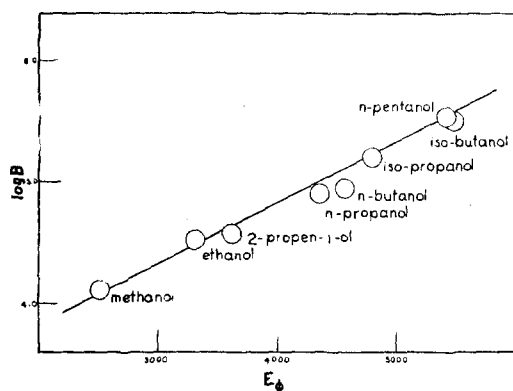


FIG. 1. Fluidity correlation for alcohols.

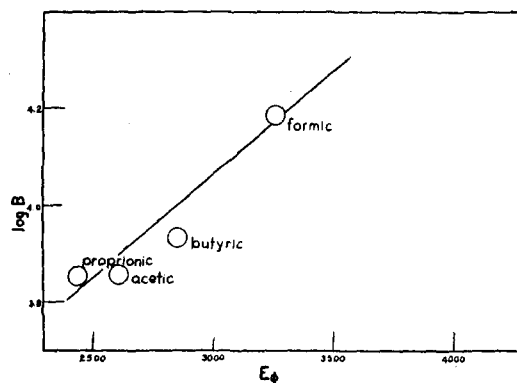


FIG. 2. Fluidity correlation for aliphatic acids.

second, hence the number of collisions leading to reaction per second. It is thus equal to the expression in Eq. (7). Substituting, one obtains

$$k_1 = \frac{n\nu}{(S-1)!} \left(\frac{E_a}{RT} \right)^{S-1} \exp(-E_{\text{obs}}/RT), \quad (11)$$

a surprisingly simple result for the rate constant of unimolecular reactions in solution.

B. Bimolecular Reactions

Bimolecular reactions in a quasi-crystalline solvent may be treated in a similar fashion. Assume that there are a molecules A and b molecules B of reactant dissolved in c molecules of an inert solvent C ($c \gg a \approx b$).

Consider now an A molecule surrounded by n other molecules. The chance that one of these is a B molecule (condition for reaction) is (approx-

mately) bn/c .† For the a molecules A ,

$$a(bn/c),$$

such pairs exist.

Now one may assume (if the masses of all the molecules are very nearly equal) that the vibrational frequency of the solvent is "impressed" on the reactant, or, alternatively, that an "average" frequency will predominate. This frequency may in any case be designated ν_C . There are then $(ab/c)n\nu_C$ vibrations per second between A and B molecules of which

$$Z_{AB(C)} = (ab/c)n\nu_C \exp(-E_\phi'/RT) \quad (12)$$

will lead to collision, and where E_ϕ' , as before, is a definite fraction of the activation energy of flow for the solvent, and where $Z_{AB(C)}$ is the collision number of A and B molecules in solvent C .

It will be observed that the above equation for

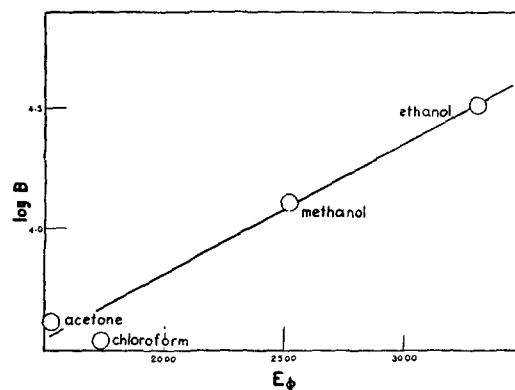


FIG. 3. Fluidity correlation.

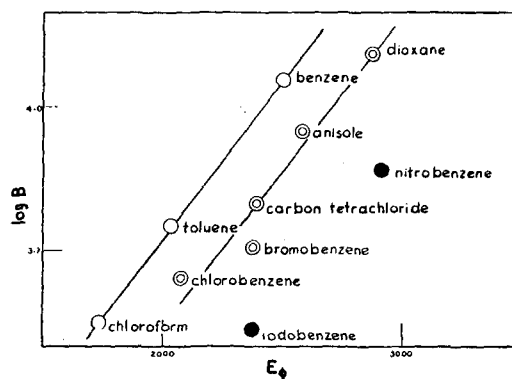


FIG. 4. Fluidity correlation.

† Exactly, of course, the probability would be $(b/a+b+c)n$; but we have assumed that c is much larger than a or b . In fact, for a 0.01M solution, c would be about 10^3a (or b).

the collision number is completely symmetrical, and that, had one started from a consideration of the probability of finding an A molecule in the coordination sphere of a B molecule, exactly the same expression would have been obtained.

From the considerations of the previous section it is clear that the number of collisions leading to reaction per second is then given by

$$(ab/c)n\nu_C \exp(-E_a'/RT) \exp(-E_a/RT) \\ = (ab/c)n\nu_C \exp(-E_{obs}/RT). \quad (13)$$

From Eq. (9) and the definition of a bimolecular reaction of second order one has

$$-da/dt = -db/dt = k_2(10^3/cV_C)ab. \quad (14)$$

Combining Eqs. (13) and (14)

$$k_2 = (nV_C\nu_C/10^3) \exp(-E_{obs}/RT). \quad (15)$$

This leads to the somewhat surprising result that *all* bimolecular reactions measured in a given solvent should have approximately the same value of the non-exponential term of the Arrhenius equation, although the relative magnitude of the

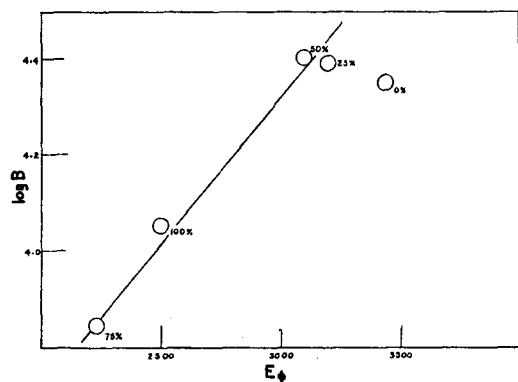


FIG. 5. Fluidity correlation ethanol + wt. % benzene.

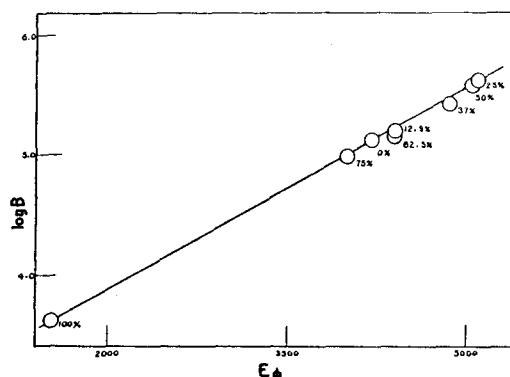


FIG. 6. Fluidity correlation water + vol. % acetone.

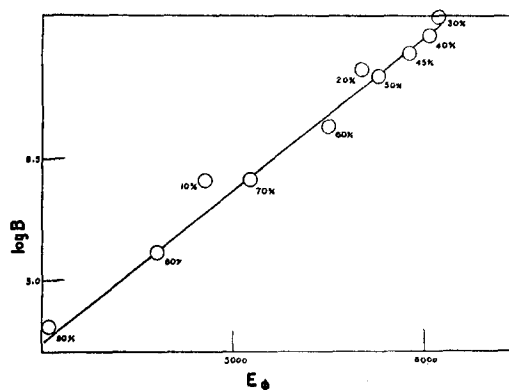


FIG. 7. Fluidity correlation water + wt. % ethanol.

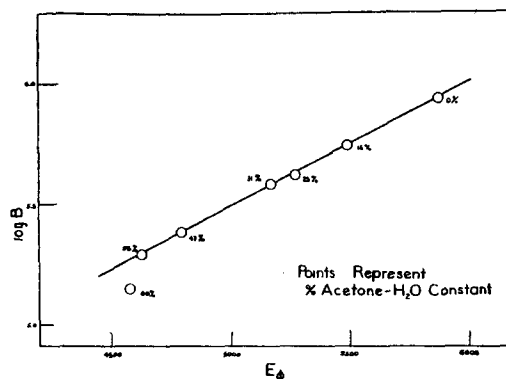


FIG. 8. Fluidity correlation system: water-acetone-ethanol. Composition of solution: 400 grams of water made up to one liter by adding acetone and ethanol. Points indicate weight percent of acetone in mixture.

forces between the various types of molecular species would be a complicating factor. Unfortunately, the experimental data recorded in the literature is somewhat too meager to justify a decision, although it would appear that this is approximately the case.

It should be mentioned that Rabinowitch,¹⁴ by considering the conditions imposed by the necessity of an A molecule *diffusing* into proximity to a B molecule, has arrived at a somewhat similar formulation: the assumption that $\nu \approx \nu_D$ is made in the estimation of an order of magnitude.

V. RELATION OF THE PARAMETERS OF THE ARRHENIUS EQUATION

Both Eqs. (11) and (15) may be written in the form

$$k = A \exp(-E_{obs}/RT),$$

¹⁴ E. Rabinowitch, Trans. Faraday Soc. **33**, 1225 (1937).

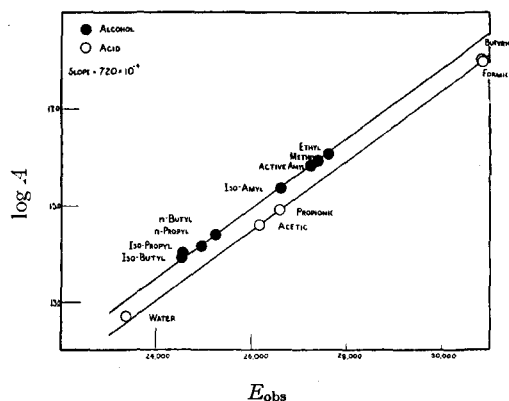


FIG. 9. Decomposition of benzene diazonium chloride.

which is the Arrhenius equation for the temperature dependence of the rate constant. Now, examination of both equations yields the interesting result that

$$A = f(\nu_c)$$

and

$$E_{obs} = F(\nu_c^2).$$

Therefore, the changes in E_{obs} and A for a given reaction measured in a series of solvents is entirely due to the change of solvent; further, it is to these very changes that we have ascribed the correlation of parameters of the fluidity equation (Eq. (3)). It may therefore be expected that *if a correlation exists between the parameters of the fluidity equation for a group of solvents, a similar correlation will exist between the parameters of the Arrhenius equation for a given reaction studied in these solvents.*

That this is actually the case may readily be shown. Figure 9 shows the correlation between

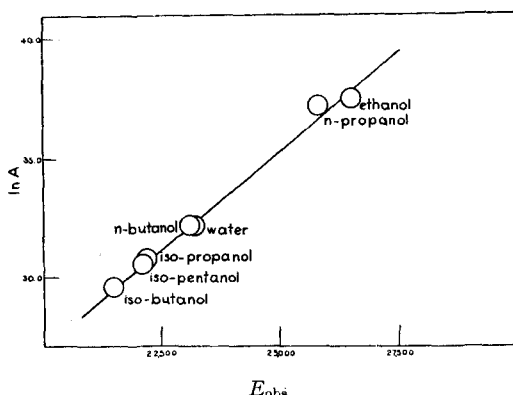


FIG. 10. Decomposition of acetone dicarboxylic acid.

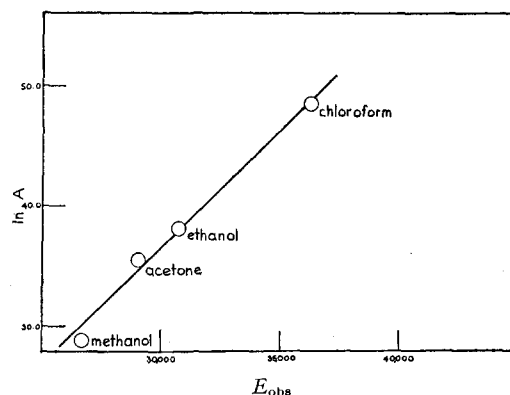


FIG. 11. Decomposition of benzylhydroxy triazolecarboxylic acid ester.

$\log A$ and E_{obs} for the decomposition of benzene diazonium chloride in a series of alcohols and acids¹⁵ (cf. Figs. 1 and 2). In Fig. 10 is shown the correlation for the decomposition of acetone-dicarboxylic acid¹⁶ in a series of alcohols (cf. Fig. 1). Figure 11 indicates the correlation for the decomposition of benzylhydroxytriazole carboxylic acid ester¹⁷ in a number of solvents (cf. Fig. 3). All of the above are unimolecular reactions.

We now turn to the case of bimolecular reactions, where the same effect is to be expected. This is shown in Fig. 12 which gives the correlation for the reaction between pyridine and methyl iodide¹⁸ for a large number of solvents.

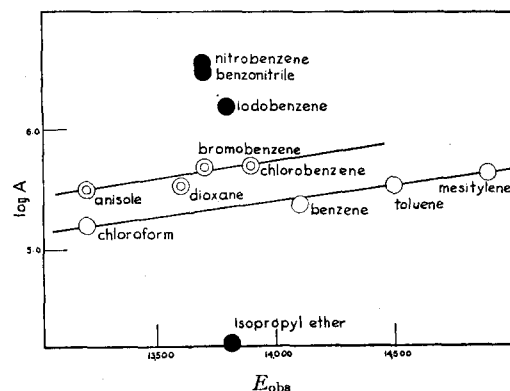


FIG. 12. Reaction of pyridine and methyl iodide.

¹⁵ Chas. E. Waring and J. Abrams. J. Am. Chem. Soc. **63**, 2757 (1941).

¹⁶ E. O. Wiig, J. Phys. Chem. **32**, 961 (1928); *ibid.* **34**, 596 (1930).

¹⁷ O. Dimroth, Annalen **373**, 367 (1910).

¹⁸ N. J. Pickles and C. N. Hinshelwood, J. Chem. Soc. **1936**, 1353.

Comparison of this plot with Fig. 4 provides a striking verification of our predictions. For example, attention was called to the fact that iodobenzene and nitrobenzene failed to correlate with the other liquids presented in Fig. 4. It is significant, therefore, that the reaction between pyridine and methyl iodide in these two solvents does not exhibit the same functional relationship as it does in those liquids in which the fluidities correlated. Unfortunately, no data for the variation of fluidity with temperature was available for benzonitrile and isopropyl ether.

Next is shown in Fig. 13 the correlation for the same reaction in a set of binary solvents¹⁹ (cf. Fig. 5). Figures 14 and 15 represent the correlation of $\log A$ and E_{obs} for the hydrolysis of benzoic and *m*-nitrobenzoic esters²⁰ in water-acetone

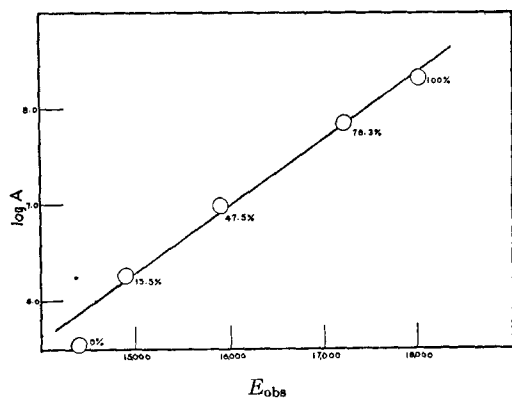


FIG. 13. Reaction of pyridine and methyl iodide in benzene + wt. % ethanol.

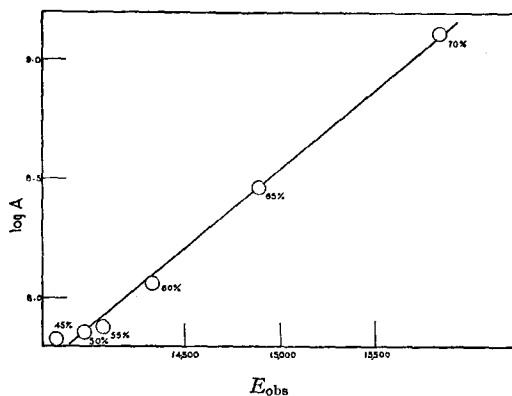


FIG. 14. Hydrolysis of benzoic ester in water + vol. % acetone.

¹⁹ R. A. Fairclough and C. N. Hinshelwood, J. Chem. Soc. 1937, 1573.

²⁰ R. A. Harman, Trans. Faraday Soc. 35, 1336 (1939).

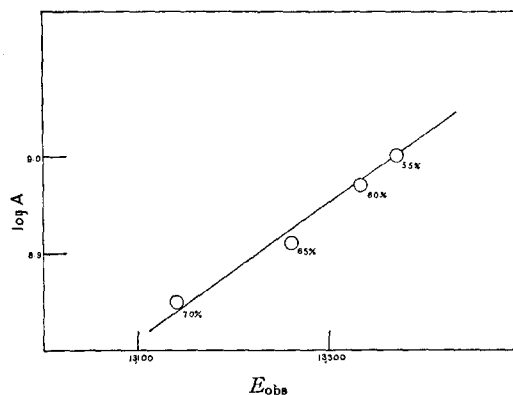


FIG. 15. Hydrolysis of *m*-nitrobenzoic ester in water + wt. % acetone.

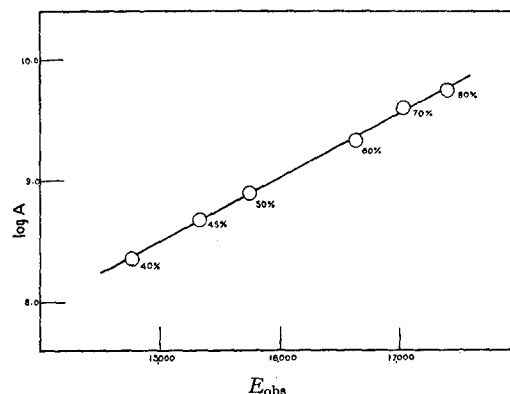


FIG. 16. Hydrolysis of benzoic ester in water + vol. % ethanol.

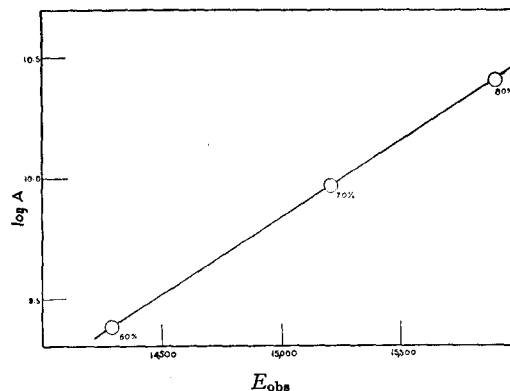


FIG. 17. Hydrolysis of *m*-nitrobenzoic ester in water + vol. % ethanol.

mixtures (cf. Fig. 6); while Figs. 16 and 17 show the same reaction in water-ethanol mixtures (cf. Fig. 7).

Figure 18 shows the correlations for the alkaline hydrolysis of benzoic ester in a set of

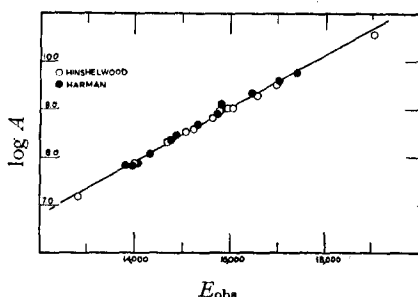


FIG. 18. Saponification of ethyl benzoate in water-acetone-ethyl alcohol mixtures.

ternary mixtures of acetone-ethanol-water^{20,21} (cf. Fig. 8).

²¹ R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.* **1937**, 538.

The existence of the correlation for the Arrhenius equation has, of course, been empirically known for some time (see, for example, references (19) and (21)), and it has been suspected that it was a solvent effect. It is quite satisfying to be able to derive it so simply from the concept of the quasi-crystalline liquid.

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Solubilization by Solutions of Long-Chain Colloidal Electrolytes*

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Increase in the concentration of a soap or other detergent does not increase the solubility of an oil above that in water until the critical concentration for the formation of micelles (*cmc*) is attained. Above this the solubility, designated as solubilization, increases and, in general, more rapidly as the soap concentration increases; i.e., per mole of soap the solubilization is greater in a 25 percent than in a 5 percent soap solution. For a homologous series the volume of oil solubilized at a constant temperature is to a first approximation inversely proportional to the molar volume. The polarity and shape of the molecules solubilized also play a role. Salts increase the extent of the solubilization; at low concentrations to an extent which may be accounted for by the increase in micellar area resulting from the depression of the *cmc* by the salt. At higher soap concentrations the increase in solubilization is greater than can be accounted for in this way.

I. INTRODUCTION

ONE of the most outstanding properties of solutions of long chain colloidal electrolytes, inclusive of soaps and many other detergents, is their ability to solubilize various organic substances. This property, utilized commercially since 1874, is of fundamental importance both in their use as detergents and in emulsion poly-

merization.¹ Engler and Dieckhoff^{1c} made very early, by the use of visual observations, a distinction between true solution and solubility in a detergent. Pickering,² in 1917, found that oils dissolve in concentrated soap solutions. Smith,³

^{1a} G. Link in Friedlander's *Fortschritte der Teerfarbenfabrikation* (1877-88), Vol. I, p. 11.

^b F. Von Heyden, D.R.P. 57842 (1890).

^c C. Engler and E. Dieckhoff, *Arch. Pharm.* **230**, 561 (1892).

^d G. A. Rappenstrauch, *Ibid.* **229**, 201 (1891).

^e R. Otto, *Ber.* **27**, 2131 (1894).

^f F. Nottbrack, *Chem. Ztg.* **32**, 100 (1908).

² S. U. Pickering, *J. Chem. Soc.* **111**, 86 (1917).

³ E. L. Smith, *J. Phys. Chem.* **36**, 1401, 1672, 2455 (1932).

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