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consideration of molecular energy magnitudes, is as good as could be expected, since the value for the liquid edge should be several times lower, and it has been found to be about half as high.

Thus, according to both Lennard-Jones and the writer the linear tension should be of the general order or 2×10^{-6} dyne. The value of 6.54 dynes

determined by Langmuir⁷ is in violent disagreement with this. While the writer has not studied the mathematics used by Langmuir, it seems obvious that the magnitude which he obtains refers to something else than the true linear tension treated in the present paper.

⁷ Langmuir, J. Chem. Phys. 1, 762 (1933).

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Factors Influencing Rates of Reaction in Solution

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The factors which may influence the rates of reactions in solution have been classified and discussed with particular reference to the effect on A in the expression $Ae^{-E/RT}$ for the rate constant K . Means by which these different effects may be studied experimentally have been discussed. An explanation has been given of the tendency of A and E to change in the same direction, and of K and E to change in opposite directions, when comparison is made of the rate of a given unimolecular reaction in various solvents.

A NUMBER of recent communications² have dealt with the factors affecting reaction rates in solution. Since the ideas have not been developed very systematically, and since (insofar as we are aware) not all possibilities have been considered, we feel that it would be useful to present a classification and discussion of these factors.

It is customary in discussing a reaction rate constant to write it in the form $K = Ae^{-E/RT}$, where E , the activation energy, is the difference between the average energy of all *reacting* molecules, pairs or triplets and that of *all* molecules, pairs or triplets. A bears a somewhat similar relation to entropy differences, as has been fully discussed in recent publications. We shall refer to the *reacting* molecule, pair or triplet, as an activated complex, using the term in the generalized sense of Rice and Gershinowitz.³ The term reactant or reactants will be used to denote the average state of the reacting system. We note the

general rule, now well understood, that anything which places a restriction upon the activated complex decreases A , while anything which places a restriction upon the reactant increases A , since (excluding any indirect effect due to a concomitant change in the energy) it makes the configuration corresponding to the activated complex *relatively* more probable. A number of authors, in considering the effect of various factors on A and K , for reactions in solution, have introduced hypothetical intermediate steps, which involve the reacting substances or the activated complex in the gas phase or pure liquid phase. It is our opinion, however, that very little of the inherent complexity of the problem is avoided in this way and we prefer to restrict our considerations to the actual reacting systems, without introduction of hypothetical processes.

With this understanding, then, we may proceed with our classification. We may divide all the influences which affect reactions in solution into two classes, as follows:

I. FACTORS WHICH ALSO OBTAIN IN GAS PHASE

Under this heading we include such matters as the orientation or freezing out of rotations into vibrations in bimolecular associations. The effect

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² Wynne-Jones and Eyring, J. Chem. Phys. 3, 492 (1935); Evans and Polanyi, Trans. Faraday Soc. 31, 875 (1935); Moelwyn-Hughes and Sherman, J. Chem. Soc. 101 (1936); Glasstone, *ibid.* 723 (1936).

³ Rice and Gershinowitz, J. Chem. Phys. 3, 482 (1935); Rice, *ibid.* 4, 54 (1936).

of such factors on A has already been extensively discussed. They can also affect E , but this is of less interest. These factors operate in the same way in solution as in gas phase (or, at least, any difference is included in the discussion below) so that it is unnecessary to go further into the matter in this communication.

II. FACTORS WHICH OBTAIN ONLY IN SOLUTION

These may again be divided into two classes:

1. The internal volume effects

A solute is not free to move through the whole volume of the solution,⁴ since a large proportion of this volume is occupied by solvent molecules. Actually only a very small fraction of the volume is available. This fact can affect (a) the translational motion, (b) the rotational motion of solute molecules. In the case of a bimolecular reaction, or one of higher order, (a) must always operate to increase A , since the translational motion takes place in a smaller volume and the collision frequency is thus increased. The factor (b) may operate in either direction, depending upon whether the rotational motion of the activated complex or that of all the molecules is the more restricted. This in turn depends to a large extent on the number of rotational degrees of freedom involved in each case. The internal volume effect may also influence the energy of activation, for we can very well imagine a change of internal volume to take place on reaction. This will require work against or by the internal pressure, with corresponding effect on the energy of reaction and hence on the energy of activation of either the direct or the reverse reaction or both. We should, perhaps, add a few words about the possible magnitude of the internal volume effect. It certainly will not be as important as other effects, but estimates from entropies of vaporization indicate that in some cases the collision number in a bimolecular reaction can be increased by a factor of 20, considering the translational effect alone.⁵ If the rotational entropy of the activated complex as compared to that of the reactant is also affected and in the same direction

⁴ See Evans and Polanyi, *Trans. Faraday Soc.* **31**, 891 (1935).

⁵ See, e.g., Rice, *J. Chem. Phys.* **4**, 371 (1936). Evans and Polanyi (reference 4) estimated a factor of 100.

the increase in A may well be by a factor between 100 and 500.

2. Solvation effects

Solvation means less freedom for both solute and solvent molecule. That is to say (since the entropy is a measure of the freedom of motion of the molecules) if the reactant or the activated complex is solvated its entropy (in which we include also the entropy of the surrounding molecules of the liquid, which are really part of the reacting system) is lowered. Now a state which has a low entropy is an improbable state, so solvation will not occur unless the *energy* of the solvated state is less than that of the unsolvated state, and sufficiently less so that the probability of the solvated state is greater. The result of this situation, in the light of our general rule regarding the effect of the entropy and the probability of reactant and activated complex on the rate of reaction, is that solvation of the reactants increases A , increases E , and decreases K (since, by the general rule, the statement of the preceding sentence is equivalent to saying that the increase in E must be more than sufficient to counterbalance the increase in A), while solvation of the activated complex has just the opposite results.*

We believe that the above list of solution effects is, for all practical purposes, exhaustive, provided, at least, that we are dealing with a pure solvent and one which does not take part in the reaction.⁶ Nevertheless, the factors are sufficiently varied and complicated, so that one may well wonder whether it will ever be possible to separate all of them experimentally. Bimolecular reactions involving complex organic substances, which have been so extensively studied in solution, are of the least favorable type from a theoretical point of view, since every one of the above factors is operative. It is therefore no wonder

* Since submission of this article for publication an article by Evans and Polanyi, *Trans. Faraday Soc.* **32**, 1333 (esp. p. 1358) (1936), containing some similar conclusions, has appeared.

⁶ The above factors are all operative in the case of a mixed solvent, but certain complications can arise which we do not wish to consider in detail in this communication. We may, however, mention what some of these complications are. In a mixed solvent we may have solvation by any of the constituents of the solvent and compound formation between constituents of the solvent (including hydration of ions when the solvent is an electrolyte solution). It is, therefore, necessary to consider equilibria involving the various constituents of the solvent, as has been pointed out by Professor A. R. Olson in discussions with one of us.

that the values of A for such reactions vary over a wide range, and it would seem to be only a coincidence that the maximum number have a value of A corresponding to that expected for simple reactions in gas phase, neglecting internal volume effects.

It would appear that the only way to obtain independent information on the internal volume effect would be to study the bimolecular association of two atoms. In this case only translational motion would be involved, orientation effects of any kind would be eliminated, and with proper selection of reactant and solvent, solvation effects might be avoided. Iodine atoms would appear to offer nearly the only possibility, but even here the experimental difficulties would certainly be great.

It seems possible, however, to obtain information concerning solvation by comparison of the velocity constants for a given reaction in various pure solvents,⁷ and also, when possible, by comparison of the reaction in solution with that in the gas phase. It seems plausible to assume that the internal volume effect will be similar for most solvents, and that the differences in reaction rate may be referred chiefly to differences in solvation. In fact, for the special case of unimolecular reactions which obey the hypothesis of exact orientation,⁸ the internal volume effect will be negligible as far as A is concerned. For it is obvious that it can have no effect upon the translational part of the entropy of activation. If the hypothesis of exact orientation applies, the rotational degrees of freedom of the complex are identical with those of the reactant, and hence the internal volume can have no effect on the rotational part of the entropy of activation.

The unimolecular decomposition of N_2O_5 has been studied both in solution and in gas phase.⁹

⁷ It should be pointed out that the effect of varying the composition of a mixed solvent is not necessarily similar to that of using different pure solvents, as will be clear from reference 6. The change of equilibria involving solvent molecules with the composition of the solvent may be such as to mask effects of the sort considered here. In addition, cases in which there is chemical reaction with the solvent, changing the nature of the reaction under consideration, must be excluded. Reaction with the solvent presumably occurs in the mutarotation of glucose, for example; thus the difference in A and E when the reaction takes place in H_2O or D_2O (Hamill and LaMer, *J. Chem. Phys.* **4**, 395 (1936)) is not covered in our discussion.

⁸ Rice and Gershinowitz, reference 3, p. 481.

⁹ Busse and Daniels, *J. Am. Chem. Soc.* **49**, 1257 (1927). Eyring and Daniels, *ibid.* **52**, 1473 (1930). For a discussion see Moelwyn-Hughes, *The Kinetics of Reactions in Solution* (Oxford, 1933), Chap. VI.

There is a number of solvents (so-called "normal" solvents) for which K , A and E are nearly identical with values for the gas phase reaction. In other solvents K is smaller, while A and E are larger than for the gas phase reaction.

The fact that a considerable number of liquids of various types act as normal solvents for this reaction suggests that the increase in activation energy due to the effect mentioned under II above is either negligible or is compensated by an increase of van der Waals forces accompanying the formation of the activated complex. Eyring and Daniels have suggested that the lower rate in abnormal solvents is due to the formation of a "complex" between the reactant and solvent molecules. The increase in E over that in normal solvents may reasonably be attributed to solvation energy of the reactant. By the above theoretical discussion (see II, 2) this should be accompanied by an increase in A and decrease in K , as is actually observed.

We may now extend the above reasoning to other examples of unimolecular reactions, assuming that the change in activation energy can be used as a measure of the amount of solvation. In the examples given by Moelwyn-Hughes⁹ it is noted that A and E for a given reaction in various solvents generally increase or decrease together, and K varies in the opposite direction. That these relations should be true without exception is not to be expected, because the change in activation energy is by no means an exact measure of the change in the amount of solvation of the reactant or activated complex.¹⁰

In the case of nitrogen pentoxide it was possible to say that the reactant molecules were the solvated ones in abnormal solvents, because the rates were lower than the gas phase rates. Unless some standard is available, it will not be

¹⁰ The parallelism between E and A has been noted by a number of writers in the past (see, e.g., Roginsky and Rosenkewitsch, *Zeits. f. physik. Chemie* **B10**, 47 (1930); *ibid.* **B15**, 103 (1931); Syrkin, *Zeits. f. anorg. Chemie* **199**, 28 (1931)), but, as far as we are aware, the explanation offered in this paper has not been presented before. We feel that it is more reasonable than the explanation of Roginsky and Rosenkewitsch, which we believe to be scarcely consistent with the more recent theories of chemical reaction. Insofar as any parallelism between E and A for different reactions exists, it seems likely that the supposition of Pollisar (*J. Am. Chem. Soc.* **54**, 3105 (1932)), that it is merely accidental, is correct. Whether the relationships noted in the data we have been considering are to some extent accidental, also, is hard to decide, but the matter needs further experimental investigation.

possible to tell whether the reactant or the activated complex is solvated, but we feel that it is probable that it will usually be the reactant.

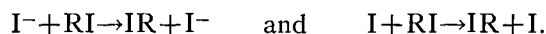
The method suggested for detecting solvation effects in unimolecular reactions, i.e., comparison of rates in various solvents, may also be extended to bimolecular reactions, and the same relations between E , A , and K , noted above, should obtain.¹¹ The available data¹² is not entirely conclusive. We may call attention to the addition reaction of ω -Br-acetophenone and aniline in various solvents. In this case it was found that the value of E is very low in benzene and chloroform as compared to various alcohols, acetone, and nitrobenzene. Corresponding to the low values of E are low values of A ; but they are *too* low and, contrary to expectations, K is very much lower in benzene and chloroform than in the other solvents. However, this reaction undoubtedly

¹¹ However, since the internal volume effect is so much more important in bimolecular reactions, its difference in different solvents may need some consideration.

¹² For a summary see Holtschmidt, *Zeits. f. anorg. Chemie* **200**, 82 (1931).

involves a labile bromine, and hence specific reaction with the polar solvents (possibly ionization) cannot be excluded.

Another possibility for investigating solvation effects in bimolecular reactions appears to lie in the comparison of metatheses involving respectively an atomic and the corresponding ionic reactant.¹³ As an example we may suggest the two optical inversions



The first of these reactions should involve extensive solvation, while in most solvents the latter should not. It is to be expected that orientation and internal volume effects should be practically identical for the two reactions.

One of us (O. K. R.) wishes to acknowledge his indebtedness to the seminar of Professor A. R. Olson, which contributed greatly to the formation of his ideas concerning reactions in solution.

¹³ In this connection see the work by Young and Olson, *J. Am. Chem. Soc.* **58**, 1157 (1936), on some ionic reactions. Note especially p. 1162.

Lattice Energies, Equilibrium Distances, Compressibilities and Characteristic Frequencies of Alkali Halide Crystals¹

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Constants in the Born and Mayer exponential expression for the repulsion between two ions have been recalculated. Using these, the lattice energies and equilibrium distances between ions have been recomputed, for alkali halide crystals. Expressions have been derived and tested for the calculation of the compressibility and the characteristic maximum infrared frequency. The relation between these two quantities is shown to be approximated by an empirical equation proposed by Madelung.

RECALCULATION OF "a," LATTICE ENERGIES AND BASIC RADII

THE average potential energy per "molecule" in a crystal composed of univalent ions symmetrically surrounded, as in structures of the NaCl and CsCl types, can be expressed^{3, 4}

¹ This paper was presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

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³ M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

⁴ M. L. Huggins and J. E. Mayer, *J. Chem. Phys.* **1**, 643 (1933).

by the equation

$$\Phi = -\frac{\alpha e^2}{r_0} - \frac{C}{r_0^6} - \frac{D}{r_0^8} + bc_+ Me^{a(r_++r--r_0)} + \frac{bc_- M'}{2} e^{a(2r_--k2r_0)} + \frac{bc_+ M'}{2} e^{a(2r_+-k2r_0)}, \quad (1)$$

where r_0 = the distance between closest ion centers, obtainable from x-ray data⁵ or from the

⁵ P. P. Ewald and C. Hermann, *Strukturbericht 1913-1928* (Akad. Verlagsgesellschaft, Leipzig, 1931).