
THE COLLISION MECHANISM AND THE PRIMARY PHOTOCHEMICAL PROCESS IN SOLUTIONS.

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(1) The Collision Number and the Collision Intervals.

The mean *number of collisions*, z (gas), of a gas molecule under NTP conditions is of the order of 10^{10} per second. The average *duration of a collision*, τ ,—*i.e.* the time during which the interaction energy is not small compared to kT —is about 10^{-13} to 10^{-12} secs. The order of magnitude of τ is the same for collisions of saturated molecules and those of free atoms or radicals. Only collisions of complicated particles possessing many degrees of freedom and low frequencies corresponding to the interchange of energy between them, can last for longer than 10^{-12} secs.

The average *collision interval* θ (gas) (because of the smallness of τ) is practically equal to $1/z$ (gas).

We now consider collisions between the molecules of a *solute* (*not* their collisions with the molecules of the solvent), and compare them with the collisions of the same molecules in the gaseous state. In the case of a strong interaction between solute and solvent, leading to the formation of solvates or of clusters of solvent molecules surrounding the dissolved particles, all the three quantities z , τ and θ may be affected by dissolution.

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In the case of a weak interaction, as presented for instance by solutions of permanent gases, or of iodine in carbon tetrachloride, the average values of z , τ and θ may remain practically unchanged. The collision duration τ , in particular, must remain unaffected by the presence of the solvent, if the interaction of the colliding particles and their kinetic energy are independent of the solvent. If, in addition, the solvation energy of a colliding pair (Fig. 1a), is not different from that of the two separated particles (Fig. 1b), then the probability of finding two given molecules in the state of collision must be the same in the gaseous and in the dissolved state. The aggregate time spent by a molecule in the collision-state during a second will therefore be the same in both cases. This total collision-time is equal to $z\tau$. With $(z\tau) (\text{sol}) = (z\tau) (\text{gas})$ and $\tau (\text{sol}) = \tau (\text{gas})$, the collision number $z (\text{sol})$ must be equal to $z (\text{gas})$ as well.

The purpose of this paper is to show that even in this ideal case of a solution which leaves the average values of z and θ unchanged, the *distribution* of collisions is changed in a significant manner. In a gas, the actual values of the collision-intervals are distributed according to the usual statistical law, the probability of an interval θ being proportional to $e^{-\theta}$. In a closely-packed medium, the collisions occur in sets. The

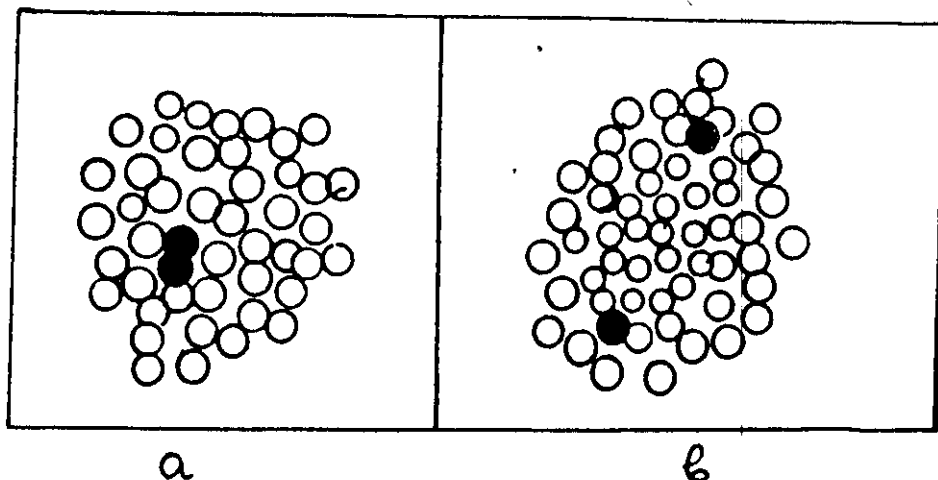


FIG. 1.

intervals θ between the collisions belonging to one set are very short, while those Θ between the sets are correspondingly longer. If the average number of collisions in a set is \bar{n} , then the average length of the inter-set intervals must be $\Theta = \bar{n}\theta_{(\text{gas})}$, in order that the total collision number z may remain unchanged.

The occurrence of collision-sets is due to the fact that the colliding pair of particles is surrounded by the molecules of the solvent and can escape from this "cage" only by a process of diffusion during which it has an opportunity of colliding several times.

To illustrate this consequence of a high concentration of the molecules in a solution, we constructed a simple model, shown schematically in Fig 2. It consists of a flat brass plate (1) with a zig-zag border (2), and an insulated knob (3) in the centre. The knob is connected to one pole of the battery, the plate itself to the other pole. A number (20-60) of small balls are distributed on the plate. All but one of them are insulated, and represent the molecules of the solvent. The one non-insulated ball and the central knob represent two dissolved molecules; every time they come into contact (as shown in the figure) a circuit is closed and the collision registered by a lamp or by an electro-magnetic recording mechanism on a drum.

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The plate is placed on a shaking machine and the balls brought into strong agitation. The zig-zag border aids in transforming the regular movement of the machine into a chaotic agitation of the balls. Fig. 3 shows two sections of the recording;

Fig. 3a was made with 25 balls on the plate; Fig. 3b with 50 balls. The "intermittent" character of the collision mechanism at high densities is clearly shown by this figure. Table I. gives the results of registering the collisions for about 10 mins. at different densities. Column (1) shows the number of the insulated balls; column (2) the proportion of the surface covered by the balls; column (5) the average number of collisions per second. Column (4), which contains the average number of collisions per set, is illustrated by Fig. 4. A comparison of columns (4) and (5) shows that whereas the total number of collisions (2) remains practically unchanged, the average length of the series (\bar{n}) increases very sharply after a certain density has been exceeded.

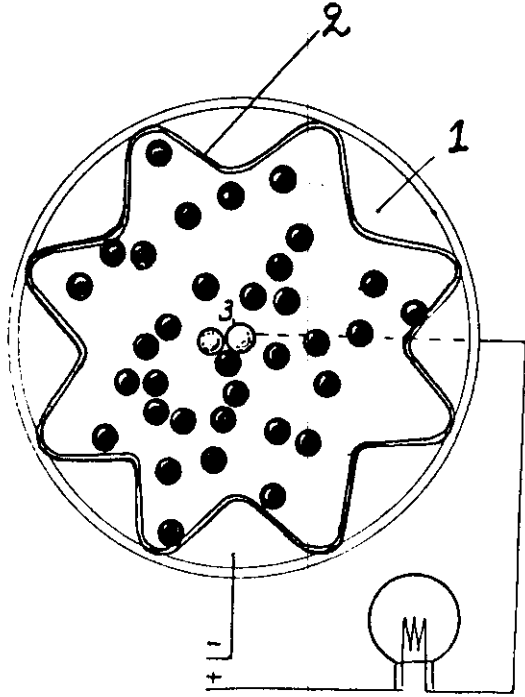


FIG. 2.

The addition of one ball to 51 causes the trebling of \bar{n} , without producing any change in z .

It is, of course, only with the greatest caution that the quantitative results obtained with this two-dimensional macroscopic model may be

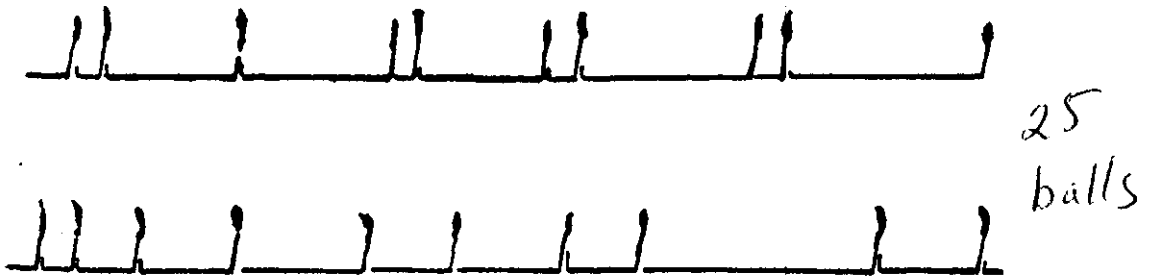


FIG. 3a.

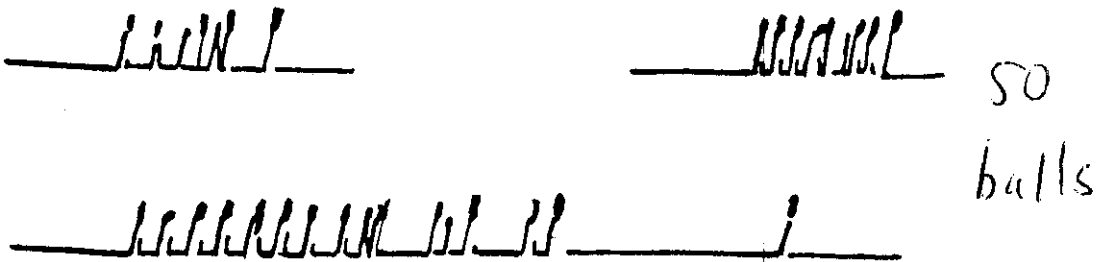


FIG. 3b.

used for real three-dimensional molecular systems. It is, however, safe to assume that in these systems also, the average length of the collision-sets increases very sharply at higher densities. The essential question is: to what section of the curve in Fig. 4 does the real liquid correspond?

TABLE I.

| N. | σ . | Number of Series with $\bar{n} =$ | | | | | | | | | | \bar{n} . | z. |
|-----|------------|-----------------------------------|----|----|----|----|----|----|----|----|--------------|-------------|------|
| | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10 and more. | | |
| 25 | 0.36 | 263 | 22 | 4 | 4 | — | — | — | — | — | — | 1.15 | 0.52 |
| 35 | 0.49 | 149 | 67 | 37 | 17 | 4 | 2 | 1 | — | — | — | 1.8 | 0.57 |
| 48 | 0.66 | 40 | 41 | 32 | 16 | 16 | 12 | 5 | 3 | 4 | 4 | 3.3 | 0.56 |
| 50 | 0.69 | 11 | 10 | 8 | 12 | 7 | 4 | 8 | 10 | 3 | 12 | 6.3 | 0.52 |
| 51 | 0.70 | 11 | 6 | 12 | 4 | 2 | 5 | 4 | 3 | 6 | 26 | 7.4 | 0.56 |
| 52 | 0.715 | 5 | 5 | — | 3 | — | 3 | 1 | — | — | 17 | 20.4 | 0.57 |
| (1) | (2) | (3) | | | | | | | | | | (4) | (5) |

If we consider, for instance, liquid argon with a molecular weight about 40 and a density 1.4, we find that 1 c.c. contains about 1.9×10^{22} molecules. The volume of an argon molecule is about 1.3×10^{-23} c.c.; the total volume of the molecules contained in 1 c.c. of the liquid is thus

0.25 c.c. In the case of CCl_4 ,

to take another example,

6×10^{21} molecules are contained in 1 c.c. of the liquid,

with an aggregate volume of

about 0.35 c.c. A *volume*

density of 35 per cent. occupied

space corresponds to a

two-dimensional density of

about 50 per cent. occupied

surface. This density produces,

according to our experiments,

collision-sets with an average

length of about 2. This estimate

of the average length of collision-

sets in real solutions is confirmed

by considerations of the diffusion

coefficients. According to Einstein

and Smoluchowski the mean displacement

Δ of a particle during the time

t is connected with its diffusion

coefficient D by the equation

$$\overline{\Delta^2} = 2Dt \quad (1)$$

In a liquid, even a displacement over a distance equal to a single molecular diameter (say $\Delta = 3 \times 10^{-8}$ cm.) is achieved on a complicated zig-zag path consisting of a great number of single segments. The statistical

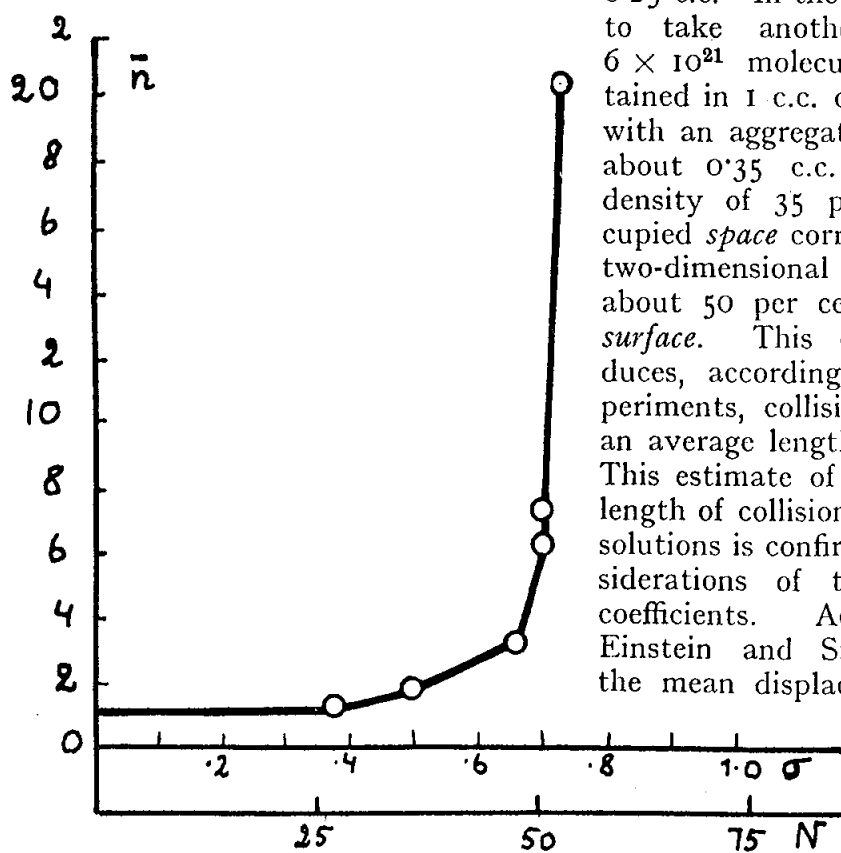


FIG. 4.

coefficient D by the equation

equation (1) can therefore be applied even to such small displacements. The diffusion coefficients of uncharged molecules in solutions of low viscosity (e.g. of iodine in carbon tetrachloride) are of the order of 2×10^{-5} . Inserting this value of D into (1) and assuming $\Delta = 3 \times 10^{-8}$ we obtain:—

$$t = 2.5 \times 10^{-11} \text{ secs.}$$

During this interval, the collision partners are agitating to and fro in a narrow space, without separating themselves so far as to allow a molecule of the solvent to slip between them. A gas molecule travelling at a speed 10^4 cm./sec. would cover a similar path, 3×10^{-8} cm., in 3×10^{-12} secs. The above calculated "separation interval," 2.5×10^{-11} secs. is ten times longer and will allow the particles to collide more than once, but probably not more than four or five times.

We may thus assume that collision-sets actually occur in solutions, but are on the average rather short, consisting of 1, 2 or 3 collisions. As confirmed by Table I., the probability of a collision-set consisting of n collisions is proportional to e^{-an} , where a is a constant depending on the density; single collisions are therefore the most frequent at all densities. Longer sets may occur in systems with higher density: highly viscous liquids, glasses or true solid phases.

The influence of the collision-sets upon the velocity of bimolecular thermal reactions was already discussed in a paper by Weiss.¹ The existence of collision-sets tends to slow down the reaction rate; but its influence can become appreciable only if the activation energy is very small—so small that the proportion $1/x$ of the number of collisions in which this energy is attained is greater than $1/\bar{n}$. In this case, the molecules which have to wait \bar{n} times longer than in a corresponding gas for their first collision, are unable to make use (statistically speaking) of all the \bar{n} collisions forming the set, because they react already after the first x collisions. For all bimolecular reactions of which the velocity can be studied experimentally, x is, however, of an order much higher than 10, and no effect of the "intermittency" of collisions can therefore be observed, at least in ordinary non-viscous solutions. In highly viscous systems the reaction velocity can be expected to decrease because of an effect of this kind.

A process in which the influence of the intermittent character of the collision-mechanism is very important is the quenching of fluorescence in liquids, because this reaction often occurs at the very first collision of the activated molecule with an appropriate partner. Wawilow and Franck² have discussed the problem of the quenching of fluorescence in solution and the influence of the viscosity from this point of view, connecting the efficiency of the quenching to the time which the quenching molecule needs to diffuse towards the activated molecule. The problem of the coagulation of sols by electrolytes was earlier treated in the same way by Smoluchowski.³ In both these cases the essential problem can be formulated as follows. At the beginning of an interval, the particles are distributed at random; how long would it take them to collide for the first time? In this paper, we are interested also in another side of the problem: supposing that the molecules are in a state of collision at the beginning of an interval—how long would it take them to reach a random

¹ J. Weiss, *Naturwiss.*, 1935, **23**, 229.

² S. I. Wawilow, *Z. Physik*, 1929, **53**, 665. J. M. Franck, S. I. Wawilow, *ibid.*, 1931, **69**, 100.

³ Smoluchowski, *Physik. Z.*, 1916, **17**, 594.

distribution? The case of "photochemical equilibrium" which is discussed in the next section, is one in which both sides of the intermittent collision-mechanism play an important rôle.

(2) The Primary Photochemical Process in Solution.

Atoms or radicals formed by photochemical dissociation in solution—*e.g.* by a process $A_2 + h\nu \rightarrow A + A$ — are, immediately after their formation, in the same position as two dissolved particles after a collision. They are in touch with each other and imprisoned in a "cage" of solvent molecules. It was pointed out in a previous paper⁴ that this situation offers the possibility of an immediate recombination of the dissociation products, called "primary recombination" to distinguish it from the "ordinary" recombination of atoms or radicals distributed at random throughout the whole body of the gas or solution. The primary recombination tends to decrease the quantum yield of dissociation below unity. Its occurrence is obviously connected with the intermittent collision mechanism discussed in Part I. If the mean number of collisions forming a set is \bar{n} , then the probability of a molecule-pair separating before a second collision has taken place is $1/\bar{n}$. It is often assumed that free atoms or radicals recombine at their first triple collision in gases, and at the very first collision in a liquid phase. Under these circumstances the probability of a freshly-formed atom-pair escaping primary recombination must be equal to $1/\bar{n}$, and the quantum yield of dissociation $\gamma = 1/\bar{n} < 1$. On the other hand, the intervals between the sets being \bar{n} times longer than the average collision intervals $\theta_{(gas)}$ in a corresponding gas, the mean "expectation of life" of an actually separated atom-pair will be $n\theta_{(gas)}$. The stationary concentration of the free atoms in the illuminated solution is given by the product of the velocity of their production and their mean life-time. The first being proportional to $\gamma = 1/\bar{n}$, and the second to \bar{n} , the concentration itself becomes independent of the occurrence of primary recombination, *i.e.* of the existence and length of the collision-sets. The kinetics of all photochemical reactions of which the velocity is proportional to the concentration of free atoms is therefore unaffected by primary recombination, and no hints as to the amount of primary recombination, can be obtained from experiments in which the stationary concentration of free atoms is measured.

This conclusion is based on the assumption that the state of the atoms or radicals formed by light absorption is not essentially different from that of the same particles meeting accidentally in solution. This is not always the case. In the above mentioned paper⁴ the *kinetic energy* of the dissociation products was considered to be essential. The absorbed light practically never exactly corresponds to the convergency limit of the band spectrum. The dissociation products possess therefore a kinetic energy in excess of the average thermal energy at room temperature. We suggested that this excess-energy makes the photochemical dissociation "explosive" and permits the products to break through the surrounding "walls" of the liquid and thus escape recombination. According to the law of conservation of momentum, however, this reasoning is correct only for the case of the dissociation products being heavier than the molecules of the solvent. Otherwise, the dissociation products, however high their kinetic energy may be, are stopped or reflected back by the first collision with a molecule of the solvent. A dependence of the primary recombination upon the amount of excess

⁴ J. Franck, E. Rabinowitch, *Trans. Faraday Soc.*, 1934, 30, 120.

energy—*i.e.* upon the wave-length of the absorbed light—may thus be expected especially in the case of solvents with very light molecules—for instance, water. As a matter of fact, a strong dependence of the quantum yield on wave-length is often observed in aqueous solutions.

In the case of a solution of iodine in carbon tetrachloride, however, no such effect of the wave-length can be anticipated, because the mass of the dissociation product ($I = 127$) is less than that of the solvent ($CCl_4 = 156$)

We have already applied this conclusion⁵ to show that neither the absolute value of the stationary concentration of free iodine atoms in illuminated iodine solutions in carbon tetrachloride and hexane, nor their independence on wave-length can be used as an argument against the occurrence of primary recombination in these solutions.

One may think that the excited electronic state $^2P_{1/2}$ of one of the iodine atoms formed photochemically may prevent it from primary recombination. No decrease in the quantum yield was, however, observed at wave-lengths longer than 5000 Å., *i.e.* in a region where the absorbed energy becomes insufficient to produce an excited iodine atom.

Summary.

1. Under certain conditions the duration of a single collision and the probability of finding two given molecules in a state of collision is the same for two molecules in solution as well as in gaseous state.

2. In this case, the total number of collisions z between dissolved molecules and the average collision interval θ are also unchanged by dissolution.

3. Even in these "ideal" solutions, an important change takes place concerning the *distribution* of the collision-intervals. *The collisions occur in sets.* The same two molecules collide several times before separating, and this collision-set is followed by a correspondingly longer "inter-set interval."

4. A mechanical model was constructed which shows the rapid increase of the average length of the sets with growing concentration of the particles. It is plausible that in ordinary non-viscous solutions the average length of the sets is of the order of 2 or 3 collisions per set—an estimate which is in agreement with the magnitude of the diffusion coefficients.

5. With average sets of \bar{n} collisions each, the probability of a colliding pair separating before a second collision takes place is $1/\bar{n}$. For atoms or radicals formed by photochemical dissociation in solution, this means a quantum yield of dissociation $\gamma = 1/\bar{n} < 1$. This decrease of the quantum yield by "primary recombination" is, however, exactly compensated by an increase in the mean life-time of free atoms (which is equal to the "inter-set interval"). The *stationary concentration* of atoms or radicals in an illuminated solution is therefore independent of the occurrence of primary recombination.

6. The kinetic energy of the products of photochemical dissociation can help them to escape primary recombination only if their mass is much larger than that of the molecules of the solvent. This is the case in some aqueous solutions, but not for instance in that of iodine in CCl_4 (which has been the object of our experimental investigations).

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⁵ E. Rabinowitch, W. C. Wood, *Trans. Faraday Soc.*, 1936, 32, 547.