

A paper presented at the Eighty-second General Meeting, held at Detroit, Mich., October 9, 1942, Malcolm Dole presiding.

REACTION RATES IN IONIC SOLUTIONS*

By P. DEBYE†

ABSTRACT

Smoluchowski's method of evaluating the fundamental frequency factor for the rate of a reaction like the coagulation of colloid suspension by employing a purely diffusional treatment is extended to include the electrostatic effects arising from the presence of net charges. The introduction of the concept of a diffuse ionic cloud and the potential calculated therefrom leads to the following results: (a) The well-established Bronsted-Debye primary salt effect formula is derived. (b) The so-called "solvent" term of the Christiansen-Scatchard equation arising from the self potential of the ions is also derived but appears as the linear approximation of an exponential expression. The conspicuous absence of quantum theory in evaluating the absolute rate of a kinetic reaction merits attention.

V. K. LaM.

The customary way followed in order to answer the question how reaction rates are influenced by electric charges which may be carried by the reacting particles is that proposed by G. Scatchard¹ following a derivation of the Bronsted²-Bjerrum³ activity relationship given by J. A. Christiansen.⁴ On the other hand, the method followed by Smoluchowski⁵ for the calculation of the rate of coagulation of colloid suspensions (within the range of rapid coagulation) can certainly be considered as a calculation of reaction rates in a special case. The fundamental question answered by Smoluchowski's treatment is: How many times per second will one of a number, n , of particles per cc. suspended in a liquid be hit by one of the others as a result of their Brownian motion? Smoluchowski obtains the desired number of collisions ν per sec. by stating that it can be calculated by solving a diffusion problem in which particles are supposed to diffuse steadily into a hole surrounding the particle in question. At the boundary of this hole the concentration is supposed to be kept 0 and at large dis-

* Manuscript received July 20, 1942.

† Professor of Physical Chemistry, Cornell University, Ithaca, N. Y.

¹ G. Scatchard, *J. Am. Chem. Soc.* **52**, 52 (1930); *Chem. Rev.* **10**, 229 (1931).

² J. N. Bronsted, *Z. physik. Chem.* **102**, 109 (1922); **115**, 337 (1925).

³ N. Bjerrum, *Z. physik. Chem.* **108**, 82 (1924).

⁴ J. A. Christiansen, *Z. physik. Chem.* **113**, 35 (1924).

⁵ Smoluchowski, *Physik. Z.* **17**, 557, 585 (1916); *Z. physik. Chem.* **92**, 129 (1917).

tances from this boundary the concentration is considered to be equal to the normal concentration n per cc. In order to take care of the Brownian motion of the central particle as well as that of all the others, the diffusion constant involved has to be taken twice as large as the normal diffusion constant δ of the particles, all considered as spheres of equal size with the diameter R . Under these circumstances the hole itself is also a sphere with a radius equal to R .

The result obtained in this way is

$$v = 8 \pi \delta R n \quad (1)$$

If the mobility of the particles is calculated, by applying Stokes' law for the motion of a sphere in a viscous liquid of viscosity η , then their friction coefficient ρ , defined as the quotient of the applied force divided by the velocity obtained, becomes

$$\rho = 3 \pi \eta R \quad (2)$$

At the same time Einstein's relation for the intensity of the Brownian motion expresses the diffusion constant δ in terms of ρ in the form

$$\delta = \frac{k T}{\rho} \quad (3)$$

in which k is Boltzmann's constant and T the absolute temperature.

Combining Eq. (2) and (3) with the fundamental relation (1) leads to the equivalent relations

$$v = \frac{8 k T}{3 \eta} n \quad (4)$$

The new form Eq. (4) shows that the number of collisions per second is independent of the size of the particles, a peculiar but well known result in colloid chemistry.

In many instances, *e.g.*, in calculating the mobility of ions or in calculating the relaxation time of dipolar molecules, it has been shown that the application of the relations of Stokes for a sphere in linear or even rotational motion to particles of molecular size leads to an estimate of the right order of magnitude. Therefore, in order to estimate the frequency factor of reaction rates in cases in which the reactions are carried out in the liquid phase, it seems advisable to use the relation, Eq. (4), instead of the customary collision theory which applies only to molecules in the gaseous state.

The independence of particle size holds only for collisions of spherical particles of equal size. If collisions between spherical particles of different sizes, say diameters R_1 and R_2 , are considered, Smoluchowski's reasoning leads to the relation

$$v = \frac{1}{4} \left(2 + \frac{R_1}{R_2} + \frac{R_2}{R_1} \right) \frac{8 k T}{3 \eta} n \quad (4')$$

However, the influence of particle size is not very important. For instance, for $R_1/R_2 = 3$, the new factor introduced in Eq. (4') is only 4/3 as compared with 1 in relation Eq. (4).

A practical example in which the validity of relation Eq. (4) can be tested is the quenching of fluorescence, *e.g.*, of fluorescein solutions by iodine ions. The result of such a comparison is very satisfactory. In this paper we are concerned with the influence of intermolecular forces on reaction rates, especially with the case in which the long-range Coulomb forces due to charges carried by the particles are preponderant. If we adopt Smoluchowski's statement about the equivalence of the diffusion problem to the collision problem, his method can easily be generalized to include the effect of a potential energy U depending on the distance between the centers of spherical particles. For particles with diameters R_1 and R_2 the final result⁶ is

$$v = \frac{\frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)}{\int_{(R_1 + R_2)/2}^{\infty} \frac{e^{U/kT}}{r^2} dr} \frac{8 k T}{3 \eta} n \quad (5)$$

In the special case $U = 0$, Eq. (5) reduces to the relation Eq. (4').

Let us now suppose that the only force to be considered is the Coulomb force between two particles of charges $z_1 \epsilon$ and $z_2 \epsilon$ in a medium of the dielectric constant D . In this case

$$U = \frac{z_1 z_2 \epsilon^2}{D} \frac{1}{r}$$

the integral occurring in Eq. (5) can be evaluated and the result becomes

$$v = f \frac{1}{4} \left(2 + \frac{R_1}{R_2} + \frac{R_2}{R_1} \right) \frac{8 k T}{3 \eta} n \quad (6)$$

This is the old result Eq. (4') except for a correction factor f represented by the formula

$$f = \frac{z_1 z_2 \epsilon^2}{D k T} \frac{2}{R_1 + R_2} \left(e^{\frac{z_1 z_2 \epsilon^2}{D k T} \frac{2}{R_1 + R_2}} - 1 \right) \quad (6')$$

The combination $z_1 z_2 \epsilon^2 / D k T$ has the dimension of a length and its

⁶ See Appendix for details of this calculation.

absolute value represents the distance at which two charges of positive valencies z_1 and z_2 have a potential energy equal to the thermal energy

kT . Consequently the characteristic quantity $\frac{z_1 z_2 \epsilon^2}{D k T} \frac{2}{R_1 + R_2}$ repre-

sents the quotient of this length divided by the distance of the centers of the particles at contact. For two univalent ions in water of room temperature the characteristic equilibrium distance $z_1 z_2 \epsilon^2 / D k T$ is 7 Ångström units. For molecules of average size the effect, therefore, is important and corresponds to a decrease in the number of collisions if z_1 and z_2 are both positive or both negative, that is, if the particles repel each other.

The assumption that the Coulomb force between the two particles considered is the only action which has to be taken into account will hold only in the limiting case of very dilute solutions. As soon as the concentration increases, the screening effect, which is fundamental for the theory of strong electrolytes, will set in. It will decrease the range of action of the forces and so counteract their influence on the frequency factor of the reaction rates.

Again the calculation can be based on Eq. (5); it is only necessary to decide upon an expression of the potential energy U as a function of the distance r . Defining the reciprocal thickness κ of the ionic layer according to the theory of strong electrolytes by the formula

$$\kappa^2 = \frac{4 \pi \epsilon^2}{D k T} \sum n_i z_i^2 \quad (7)$$

this potential energy can be expressed in the form

$$U = \frac{1}{2} \left\{ \frac{e^{\frac{\kappa R_2}{2}}}{1 + \frac{\kappa R_1}{2}} + \frac{e^{\frac{\kappa R_1}{2}}}{1 + \frac{\kappa R_2}{2}} \right\} \frac{z_1 z_2 \epsilon^2}{D k T} \frac{e^{-\kappa r}}{r} \quad (8)$$

at least for large distances r . Since the main effect of the concentration occurs at larger distances where the familiar decrease proportional to $1/r$ is materially changed by the occurrence of the exponential factor $e^{-\kappa r}$, it can be expected that the introduction of the approximate expression Eq. (8) for the energy will be adequate for the calculation of the concentration effect, at least for small concentrations which are according to Eq. (7) related to small values of κ .

The integral appearing in Eq. (5) now is more complicated and cannot be expressed by a simple function. A similar integral appears in the theory of the influence of strong electrolytes on the surface tension. For our immediate purpose it may suffice to indicate the result in the limit for small values of κ .

In this case the number of collisions ν per second can again be expressed by an equation similar to Eq. (6); it is only necessary to replace the correction factor f by another factor f^* . If we introduce the equilibrium distance l by putting

$$\frac{z_1 z_2 \epsilon^2}{D k T} = l \quad (9)$$

and furthermore the thickness of the ionic layer λ as

$$\lambda = \frac{1}{\kappa} \quad (10)$$

the former correction factor f as expressed by Eq. (6') is

$$f = \frac{2l}{R_1 + R_2} \left/ \left(e^{\frac{2l}{R_1 + R_2}} - 1 \right) \right. \quad (11)$$

The new correction factor f^* becomes

$$f^* = \gamma \frac{2l}{R_1 + R_2} e^{\gamma \frac{l}{\lambda}} \left/ \left(e^{\gamma \frac{2l}{R_1 + R_2}} - 1 \right) \right. \quad (12)$$

with

$$\gamma = \frac{1}{2} \left\{ \frac{e^{R_1/2\lambda}}{R_1} + \frac{e^{R_2/2\lambda}}{R_2} \right\} \left/ \left(1 + \frac{R_1}{2\lambda} + 1 + \frac{R_2}{2\lambda} \right) \right. \quad (12')$$

In the limit for very small concentrations (λ being infinite) γ becomes equal to unity and f^* becomes identical with f .

Finally f^* can be developed in powers of κ or $\frac{1}{\lambda}$. If this is carried out and if only the term proportional to the first power of κ is retained, the result can be simply expressed by stating that

$$\frac{f^*}{f} = 1 + \kappa l = 1 + \frac{l}{\lambda} \quad (13)$$

since the difference of γ from unity is of the second order in κ . The results here obtained are very similar to those published in the litera-

ture; a comparison can be most easily made by referring to the book of Glasstone, Laidler and Eyring on the Theory of Rate Processes, page 423 and following.

In detail, significant differences exist, for instance, with respect to the absolute value of the rate constants. The main advantage seems to be that the proposed treatment translates the physical picture of the processes involved into the necessary formulas without the help of any intermediary.

APPENDIX

If ρ_1 and ρ_2 are the friction constants for the two kinds of particles of diameters R_1 and R_2 , which have to be considered, the diffusion equation takes the form

$$\frac{I}{4\pi r^2} = -(\delta_1 + \delta_2) \frac{dn}{dr} - \left(\frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \frac{dU}{dr} n$$

δ_1 and δ_2 are the diffusion constants and I is the specific current, that is, the number of particles passing through one square centimeter per second under the influence of the combined effect of an established concentration gradient and the forces between the particles. According to Einstein's theorem δ_1 and δ_2 can be replaced by the expressions kT/ρ_1 and kT/ρ_2 . A general solution of the equation now is

$$n = - \frac{I}{4\pi kT} \frac{e^{-U/kT}}{\frac{1}{\rho_1} + \frac{1}{\rho_2}} \int \frac{r}{e^{-U/kT}} \frac{dr}{r^2}$$

In order that $n = 0$ at the boundary of the central sphere with a radius equal to $(R_1 + R_2)/2$, the lower limit of the integral has to be taken equal to $r = (R_1 + R_2)/2$. On the other hand, in order that for $r = \infty$ the concentration becomes equal to the overall concentration, which for our immediate purpose shall be called n_0 , the condition

$$n_0 = - \frac{I}{4\pi kT} \frac{1}{\frac{1}{\rho_1} + \frac{1}{\rho_2}} \int_{(R_1 + R_2)/2}^{\infty} e^{-U/kT} \frac{dr}{r^2}$$

has to be satisfied, since the energy function U has been normalized to become zero at infinite distance. Applying Stokes' law means replacing ρ_1 and ρ_2 by $3\pi\eta R_1$ and $3\pi\eta R_2$ respectively, and since the total current, I , is identical with the number of impacts ν as defined in the text, our result is identical with Eq. (5).

Resumen del artículo: "Velocidad de Reacción en Soluciones Iónicas"

Smoluchowski ha derivado fórmulas que dan el número de choques entre partículas coloides del mismo tamaño (ecn. 4), y de tamaños diferentes (ecn. 4'). Se basan en la suposición de que la frecuencia de los choques depende de la velocidad de difusión de las partículas hacia un agujero que rodea la partícula que se considera. Aplicando esta idea a una nube difusa de iones se deriva la ecuación Bronsted-Debye del efecto de concentración sobre la actividad. Se puede derivar la velocidad de una reacción sin emplear la teoría de los cuantos.

DISCUSSION

P. DEBYE: Then you find you can quench those solutions. One of the molecules takes up a quantity of light, goes around with this quantum for a certain time, and then makes up its mind to give this quantum off and give you some light again, but some atoms, for instance, in the case of fluorescence, iodine ions, have the property of robbing these molecules of their quantum. Then you have the fluorescent molecule that goes around and has this quantum in its pocket and wants to give it off but, before it can do so, this iodine ion comes and robs the molecule, and that is the quenching effect. And so you have here encounters between iodine ions and fluorescent molecules, which are also ions. For instance, in the case of quinine sulfate the molecules have a double positive charge, and if you want to know how the intensity of fluorescence depends on the concentration of your quenching, you have the same problem, and I am talking here about how many times one of these ions will meet one of the fluorescent molecules. You can make that experiment a little bit better still. You can put into the solution containing your fluorescent molecules and your iodine ions some neutral salt such as KNO_3 . Then the neutral salt, which increases the ionic strength of the solution, is going to screen your particles, quinine here, iodine there, which are forced toward each other. As soon as you put more neutral salt into the solution, they are going to be surrounded by screens of ions, and, therefore, the forces will be changed.

K. FAJANS⁷: One finds different definitions of the thickness of the ionic atmosphere. What do you mean by 100 Å for a 0.001 *M* solution of a mono-monovalent electrolyte?

P. DEBYE: In an electrolytic solution the electric potential at a distance *r* of a charge is not proportional to $1/r$ but to $e^{-\kappa r}/r$. By its exponential factor this formula describes the shielding of the action of the central charge by the diffuse ionic layer (with an average charge of opposite sign) which surrounds it and in which the electric density distribution is a result of the dynamic equilibrium between the attractive and repulsive forces of electrical origin and the thermal motion. The reciprocal of κ called λ in my paper is the length, which I called the thickness of the ionic layer.

K. FAJANS: In a paper presented with Mr. Johnson,⁸ we try to obtain experimental evidence for the nearest distance between oppositely charged ions in solution. If your theory leads to a thickness of 100 Å, would you expect an appreciable number of ions to approach each other as closely as 5 Å?

P. DEBYE: At a distance of only 5 Å the difference between the number of negative and positive charges is much more effective, of course.

K. FAJANS: But you will find ions as close as that?

P. DEBYE: Oh, yes.

J. C. WARNER⁹: I think this paper by Dr. Debye is extremely interesting and shows again his genius for starting with quite simple physical concepts to give us something of importance. After first seeing his paper, I think I must have had

⁷ Professor of Chemistry, University of Michigan, Ann Arbor, Mich.

⁸ See page 273 this volume.

⁹ Head, Dept. of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pa.

the same reaction that many other people had; we wonder why someone didn't do it before.

Dr. Debye, what is the effect of the viscosity on the frequency of collisions? As far as I know, it is not very important as regards reaction rates in solution and I, personally, have not been able to find any correlation between viscosity and reaction rate. Would you care to comment on that?

P. DEBYE: Reaction rates depend on two things: (1) It is important to know how many times per second the reacting particles come near enough to each other in order to be able to react. (2) We have to know what the probability is that at that time the particles will be in such an activated state that the reaction really occurs. I have discussed only the former. If the activation energy is relatively large, the temperature coefficient will be determined to a large extent by the activation energy alone. Only in cases where this energy is small should the effect of the viscosity on the number of impacts become detectable. If we were to interpret the viscosity effect in water in terms of an activation energy, this would amount to about 4.5 or 5 kilo-calories.

J. C. WARNER: Dielectric constant is also an exponential function, and therefore its change with temperature also contributes to the classic Arrhenius activation energy, as I have pointed out elsewhere.

P. DEBYE: Yes, but you know that the dielectric constant does not change very rapidly with temperature, whereas viscosity does. Stoughton and Rollefson¹⁰ also showed that the dielectric constant enters into this picture. In their experiments they changed the dielectric of the surrounding water to the dielectric of dioxane through a series of aqueous solutions of dioxane of different concentrations.

¹⁰ J. Am. Chem. Soc. **62**, 2264-8 (1940).