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## Application of the Diffusion Theory to the Bimolecular Reactions

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The solution of the nonlinear diffusion equation describing the process of recombination can be reduced to the solution of two more common equations—one linear diffusion equation without the recombinational member and one nonlinear equation which can be easily integrated. The proportion of recombinations between “congeneric” and “foreign” pairs, i.e., the role of monomolecularity or bimolecularity in the recombination process, is taken into account automatically by the initial conditions. In the later stage (if the excitation is uniform over the whole volume) the recombination process is simply bimolecular. At the decrease of the excitation the monomolecularity increases but never reaches a value of 100%. In the case of the stationary weak excitation the concentration of divided particles is proportional to the square root of the intensity of the excitation.

IN recent years a number of papers appeared<sup>1</sup> about the investigation of the temperature annealing of radiation defects. In order to interpret the time dependence of this phenomenon the diffusion theory is applied, because of the fact that the radiation defects, i.e., vacant sites and interstitial ions or atoms, can move in the crystal lattice. Since there are two kinds of defects which recombine by encounters, the diffusion equation becomes nonlinear owing to the presence of the nonlinear recombination term. The situation is further complicated by the fact that the recombination is also partially monomolecular. The difficulty is that radiational defects are created in pairs—i.e., simultaneously as a vacancy and an interstitial ion or atom—the distance between them being relatively small. As a consequence of this, their reunion (recombination) becomes very probable and there is a lower probability for their separation followed by recombination with the components of “foreign” pairs.

A quite similar problem was considered much earlier in connection with recombinational luminescence—when during phosphor excitation, photoelectrons and ionized luminescent centers arose (in pairs) and then recombined.<sup>2</sup> However, this apparently was not known to the authors of the papers in reference 1.

In reference 2 the diffusion nonlinear equation was derived, taking into account the peculiarities of electron behavior near the ionized luminescent centers.<sup>3</sup> The physical results obtained from this earlier equation are identical with those obtained from Waite's equation<sup>1</sup> for reacting particle pair distributions after he has applied the superposition approximation to triplet distributions and neglects correlation between non-reacting pairs of particles. This equation is of spherical symmetry, because the motion of the electron is considered relative to the ionized centers. The electron distribution is described by the function  $n_{rt}$ , where  $r$  is the distance of the electron from the center, and  $t$  is the time. At large distances  $n_{rt}$  coincides with the average electron concentration  $n_t$ , i.e.,

$$n_{rt} \rightarrow n_t \quad \text{when } r \rightarrow \infty. \quad (1)$$

It is convenient to introduce the following quantity:

$$\eta_{rt} = n_{rt}/n_t, \quad (2)$$

the relative electron concentration. It is found that with the help of (2), and taking (1) into account, the solution of the nonlinear diffusion equation for  $n_{rt}$  can be reduced to the solution of a linear equation (!) for

<sup>1</sup> E. L. Brown and R. C. Fletcher, *Phys. Rev.* **92**, 591 (1953); T. R. Waite, *Phys. Rev.* **102**, 463, 471 (1957); *J. Chem. Phys.* **28**, 103 (1958).

<sup>2</sup> V. V. Antonov-Romanovsky, *Trudy Fiz. Inst. Akad. Nauk*

*S.S.S.R.* **2**, 157 (1942). V. V. Antonov-Romanovsky, *J. Phys. (U.S.S.R.)* **6**, 120 (1942); **7**, 153 (1943).

<sup>3</sup> See also V. V. Antonov-Romanovsky, *Optika i Spektroskopiya* **3**, 592 (1957).

$\eta_{rt}$  without the recombinational term,

$$\frac{\partial \eta_{rt}}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \eta_{rt}}{\partial r} \right) - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r \eta_{rt}), \quad (3)$$

where  $D$  is the diffusion coefficient and  $u_r$  is the electron drift due to the force field of the ionized center. The average electron concentration  $n_t$  is then given by

$$n_t = n_0 \left/ \left( 1 + n_0 \int_0^t p_t dt \right) \right., \quad (4)$$

$$p_t = -4\pi r_0^2 D (\partial \eta_{rt} / \partial r)_{r=r_0},$$

where  $n_0$  is the initial mean electron concentration and  $r_0$  is the radius of the recombinational sphere. The initial conditions for (3) are

$$\eta_{rt} = \eta_{r0}' + \varphi_{r0}' / n_0 \text{ for } t=0 \text{ and } \eta_{rt} = 0 \text{ for } r=r_0, \quad (5)$$

where  $\eta_{r0}'$  and  $\varphi_{r0}'$  are the initial distribution of the "foreign" electrons and the "original" electron, respectively. In excitation of short duration during which the electrons have no time to be noticeably displaced and to recombine,

$$\eta_{r0}' = 1 \quad \text{and} \quad 4\pi \int_{r_0}^{\infty} \varphi_{r0}' r^2 dr = 1, \quad (6)$$

if one supposes that the luminescent centers are distributed statistically and direct ionization takes place.

It follows from the above that the bimolecular or monomolecular character of kinetics is determined by the first of initial conditions (5). In the case of strong excitation, when  $n_0$  is large, the bimolecularity increases; in the case of low excitation the monomolecularity increases. But during the later stages when  $t \rightarrow \infty$ , independently of the initial conditions, the value  $\eta_{rt} \rightarrow \eta_{r\infty} = \text{const}$ ; then it follows from (4) that

$$n_t = n_0 / (1 + n_0 p_0 t), \quad (7)$$

where

$$p_0 = 4\pi r_0^2 D (\partial \eta_{r\infty} / \partial r)_{r=r_0}. \quad (8)$$

Thus, independently of the initial conditions, during the later stages,  $n_t$  always decays as a hyperbola of the first order, i.e., the kinetics of relaxation becomes completely bimolecular.

If the recombining particles are charged, i.e., if they take additional charge  $+e$  or  $-e$  relative to the lattice, a question can arise, naturally, about the influence of the diffusion and attraction on the recombination rate.

We shall consider first the stationary case when, in (3),  $\partial \eta_{rt} / \partial t = 0$  and therefore  $\eta_{rt} = \eta_{r\infty}$ . If we put as usual

$$u_r = -\lambda / r^2, \quad (9)$$

where

$$\lambda = e\mu / \epsilon_0, \quad (10)$$

$\mu$  being the mobility coefficient and  $\epsilon_0$  the dielectric constant (we neglect the possible peculiarities in the particle motion when  $r$  is small), then we obtain from (3) and (4):

$$\eta_{r\infty} = 1 - (e^{\lambda/Dr} - 1) / (e^{\lambda/Dr_0} - 1) \quad (11)$$

and

$$p_\infty = 4\pi\lambda / (1 - e^{-\lambda/Dr_0}). \quad (12)$$

It follows from (12) that, for  $\lambda/Dr_0 \ll 1$ ,

$$p_{\infty D} \approx 4\pi Dr_0, \quad (13)$$

i.e., as if only pure diffusion takes place. If  $\lambda/Dr_0 \gg 1$ , we obtain

$$p_{\infty \mu} \approx 4\pi\lambda, \quad (14)$$

i.e., as if there is only pure attraction. That means that the value  $\lambda/Dr_0 \approx 1$  is a critical one. We will estimate the value of  $r_0 = R$  at which this condition will be fulfilled.

According to Einstein's formula,

$$D/\mu = kT/e. \quad (15)$$

Then by taking (10) and (15) into account, we obtain from the condition  $\lambda/DR \approx 1$ , that ( $kT \sim \frac{3}{2}kT$ )

$$e^2/\epsilon_0 R \sim \frac{3}{2}kT. \quad (16)$$

This means that  $R$  is a distance at which the potential energy of two mutually acting components becomes equal to their average kinetic energy. Thus the critical distance  $R$  coincides in magnitude with the radius of the capture sphere of the mutually influencing components. It follows from (16) that at room temperature

$$R \sim 10a, \quad (17)$$

where  $a$  is the lattice constant ( $a \sim 5 \times 10^{-8}$  cm).

The radius of the recombinational sphere is

$$r_0 \sim a; \quad (18)$$

therefore  $r_0 \ll R$  and the role of diffusion is considerably less important than the role of attraction. On the other hand, it means that in the case of uncharged particles the speed of recombination would be much smaller (other conditions being equal). A more precise analysis shows that in the case of the charged particles at room temperature and stationary conditions, the role of diffusion in the recombination nevertheless can not be absolutely neglected ( $p_{\infty D} \sim 0.1\mu$ ). Therefore, during the initial stages of the relaxation process, when the number of the closely arranged components (of different signs) can substantially exceed the number that will be given by the statistical distribution (i.e., when we have a large concentration gradient), the diffusion role might dominate.

In connection with the fact that the attraction (if we exclude the initial stages) plays the main role, a question arises—can the interaction of charged particles (of both signs) noticeably change the diffusion coefficient?

The calculation shows that the diffusion coefficient increases,

$$\Delta D \sim R/\bar{r}, \quad (19)$$

where  $\bar{r}$  is the mean distance between the particles. Owing to the fact that usually  $\bar{r} \gg R$ , we obtain that  $\Delta D \ll D$  and therefore we can neglect such an increase. Thus in this case also, the value  $R$  plays the role (but a different one) of a "critical" distance.

If the "original" electron (particle) distribution function  $\varphi_{r0}'$  is known, the distribution function  $\eta_{r\infty}$  at a stationary excitation can be found from the following equation:

$$\frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \eta_{r\infty}}{\partial r} \right) - \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r \eta_{r\infty}) + \frac{\kappa E}{n_\infty} \left( 1 + \frac{\varphi_{r0}'}{n_\infty} - \eta_{r\infty} \right) = 0, \quad (20)$$

where  $E$  is the exciting intensity,  $\kappa$  is proportional to the absorption coefficient,  $n_\infty$  is the concentration of recombining particles, and

$$\eta_{r\infty} \rightarrow 1 \text{ as } r \rightarrow \infty \text{ and } \eta_{r\infty} = 0 \text{ for } r = r_0. \quad (21)$$

The magnitude  $p_\infty$  can be estimated as before from (4). On the other hand, because of the fact that in the stationary state the number of recombinations is equal to the number of ionizations, one has

$$p_\infty = \kappa E / n_\infty^2. \quad (22)$$

We can point out that contrary to (20), the formula for a nonstationary excitation becomes nonlinear.

From (20), by the way, one can obtain the following interesting result. Even for  $E \rightarrow 0$  when the monomolecularity seems to be dominant, the accumulating light sum

$$n_\infty \sim \sqrt{E}. \quad (23)$$

However, such striking results (pure bimolecular accumulation) find their explanation in the fact that some part of the "congeneric" components diverges at an infinitely large distance.

Thus a problem was considered which is in some aspect more complicated (since the attraction is taken into account) than in the investigation of the temperature annihilation of radiation defects. Therefore the present paper might prove to be useful for investigators working in this field.

## High-Voltage Glow Discharges in D<sub>2</sub> Gas. II. Cathode Fall Theory\*

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A one-dimensional theoretical treatment of the cathode fall region of 40–100 kv glow discharges in D<sub>2</sub> gas is presented. The region is assumed to be fed with an external supply of slow D<sub>2</sub><sup>+</sup> ions from an adjoining plasma at one boundary and an influx of secondary electrons from a cathode forming a second boundary. As a function of the current density of plasma ions the following quantities are calculated: the energy distributions and fluxes of D<sup>+</sup>, D<sub>2</sub><sup>+</sup>, and D particles incident on the cathode, the cathode electron current, the thickness of the cathode fall region, the ratio of cathode fall electron current to plasma ion current, the potential distribution including the effect of positive-ion space charge, and the voltage vs current characteristics for a fixed cathode fall thickness. The theoretical results are compared with the experimental results of Part I. Using the available cross-section data from the literature, account is taken of D<sub>2</sub><sup>+</sup> charge exchange and dissociation, electron capture by D<sup>+</sup>, electron loss from D, ionization of the gas by fast D<sup>+</sup>, D<sub>2</sub><sup>+</sup>, and D, and ionization by cathode secondaries. Arbitrary approximations are made to a few of the unknown cross sections.

### I. INTRODUCTION

**P**ART I<sup>1</sup> of this series described several diagnostic experiments on glow discharges in deuterium gas at applied potentials of 40 to 80 kv and currents of the order of 1 amp. These discharges were found to be composed of a plasma-filled region occupying about half the interelectrode space and a cathode fall region extending from the plasma to the cathode. Virtually the entire applied potential was found to appear across the cathode fall region.

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<sup>1</sup> G. W. McClure, Phys. Rev. 124, 969 (1961).

Sufficient information was obtained from the analysis of the diagnostic measurements to determine the types of collision processes and modes of particle motion in both regions of the discharge. In the present paper the cathode fall region is treated theoretically in a one-dimensional approximation taking into account as fully as possible the numerous cathode fall collision processes discussed in Part I. Rigorous account is taken of the connection between the potential distribution and positive-ion space charge. The quantities derived include the energy distribution of the ions and fast neutrals incident on the cathode, the length of the cathode fall region, the potential distribution along