

THE MATHEMATICS OF STEADY-STATE DIFFUSION AND FLOW TUBE SYSTEMS
II. Measurement of Discharge-Zone Rate Parameters

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I. INTRODUCTION

The techniques used to measure the rate of a chemical reaction or to determine the physical characteristics of a chemical compound are dictated by the physical and chemical properties of the compound, particularly by its lifetime and reactivity in relation to its chemical environment. This environment can be chosen to maximize the interactions between the compound and other materials (a reaction environment) or else to minimize such interactions (an isolation environment). Progress in chemistry has been dependent upon the skill chemists have shown in selecting the appropriate reaction or isolation environments.

The problem of developing suitable isolation environments has been a difficult one in the study of flames, shock waves, explosions, and electrical discharges, where the chemical intermediates -- ions, electrons, atoms, free radicals, excited atoms, excited molecules, excited ions, and metastable molecules -- are highly reactive and have extremely short lifetimes. Notable advances along these lines have been the matrix isolation technique developed by Pimentel and co-workers, contacting the intermediates with a very cold surface, and the use of materials that deactivate surfaces against the recombination of atoms and free radicals.¹⁻⁷ None of these techniques have yet been successful in significantly prolonging the lifetime of an ion.

This problem can be circumvented by the expedient of placing a source of the chemical intermediates in close proximity to a sink and optimizing the rates of loss and transport of the highly reactive species between these two regions. The most popular source-sink system for the study of gas-phase kinetics of neutral molecules is the diffusion or flow tube, which usually employs an electrodeless discharge as the source.^{9,10} Such systems have also been used with considerable success in the field of plasma chemistry for the experimental measurement of associative detachment and ion-neutral reaction rates.^{11,12}

The simplicity of these systems is deceptive -- they are usually quite complex. To illustrate this point, Table I gives a non-exhaustive list of rate processes occurring within the system shown in Fig. 1.²⁴ It is clear that a comprehensive mathematical description of such systems is desirable not only to aid in the choice of experimental conditions and assessment of experimental data, but also to guide those who use diffusion or flow tubes or the measured rate parameters.

Most theoretical descriptions of a diffusion or flow tube have ignored the source of reactive species -- the electrical discharge -- by the assumption of a specified value for the reactive specie concentration at the discharge-zone boundary.¹³⁻¹⁷ Tsu and Boudart were the first to incorporate the discharge zone in the derivation and the author has elaborated upon this type of theoretical

description for both diffusion and flow tubes.¹⁸⁻²⁰

In the present paper, it is shown that these new equations provide the missing link between the theoretical expressions characterizing the electron and ion concentration distributions within a discharge zone and the expressions typically used for describing the gas-kinetic reactions of the discharge products.^{21-23,30} Suggestions are given on how averaged first-order rate constants for the production of discharge products can be measured and how they can be used to calculate the steady-state concentrations of neutral species at any point within the reaction tube. In certain cases, relatively modest equipment can be used to perform such measurements.

The numbering of equations in the present paper continues a previous sequence.¹⁹

II. RATE EXPRESSIONS

A. Neutral Species

Consider a binary system of atoms and the parent molecules present within a long cylindrical tube that has two zones -- a discharge zone and a reactor zone (Fig. 1). If the walls of the tube are not too active, if there are no three-body recombination reactions, and if the atom concentration is less than 15%, the mass-balance equations for the atoms become¹⁹

$$D_{12} \frac{d^2 c_1'}{dz^2} - v_z \frac{dc_1'}{dz} + k_0'(c - c_1') - k_1' c_1' = 0 \quad (1)$$

diffusion convection atom production first-order
atom loss

for the discharge zone and

$$D_{12} \frac{d^2 c_1}{dz^2} - v_z \frac{dc_1}{dz} - k_1 c_1 = 0 \quad (2)$$

diffusion convection first-order
atom loss

for the reactor zone. These equations can be rewritten in dimensionless form,

$$\frac{d^2 \eta}{d\lambda^2} + \beta \frac{d\eta}{d\lambda} + \sigma^2(1 - \eta) - \frac{\eta}{\delta'^2} = 0 \quad (6)$$

and

$$\frac{d^2 \psi}{d\lambda^2} + \beta \frac{d\psi}{d\lambda} - \frac{\psi}{\mu^2} = 0 \quad (7)$$

In a previous paper, a total of 36 equations summarized the operation of a flow or diffusion tube, with or without a first-order atom loss process in the reactor zone, for three different discharge-zone boundary conditions and three different end-plate boundary conditions.¹⁹ The solutions to Eq. (7) were sub-

divided into four cases:

- Case I. Diffusion tube ($\beta = 0$) with inactive reactor zone walls ($1/\mu^2 = 0$);
 Case II. Diffusion tube ($\beta = 0$) with active reactor-zone walls ($1/\mu^2 \neq 0$);
 Case III. Flow tube ($\beta \neq 0$) with inactive reactor-zone walls ($1/\mu^2 = 0$); and
 Case IV. Flow tube ($\beta \neq 0$) with active reactor-zone walls ($1/\mu^2 \neq 0$).

The eight most useful solutions are listed in Table II. The most general solution for the reactor zone, from which the 35 others can be obtained by appropriate simplifications, is Eq. (60). The original paper should be consulted for further information concerning the derivation of the mass-balance equations, the boundary conditions, or the other theoretical solutions. Definitions of dimensionless groups are given in the Appendix.

TABLE II. Pertinent Solutions to Equation (7).

End-plate Boundary Conditions:	Discharge-zone boundary condition: $\frac{d\eta}{d\lambda} = 0$ at $\lambda = \frac{L+M}{R}$			
	Case I.	Case II.	Case III.	Case IV.
$\frac{d\psi}{d\lambda} = 0$ at $\lambda = -\infty$	Eq. (27)	Eq. (36)	Eq. (27)	Eq. (54)
$\frac{d\psi}{d\lambda} = \frac{\psi}{\xi'}$ at $\lambda = 0$	Eq. (33)	Eq. (42)	Eq. (51)	Eq. (60)

$$\psi = \sigma^2 \delta^2 \quad (27)$$

$$\psi = \sigma^2 \delta^2 \frac{\lambda + \xi'}{L/R + \xi' + \delta \coth(M/\delta R)} \quad (33)$$

$$\psi = \sigma^2 \delta^2 \frac{e^{-z/\mu R}}{1 + \delta/\mu \coth(M/\delta R)} \quad (36)$$

$$\psi = \sigma^2 \delta^2 \frac{H e^{\lambda/\mu} + e^{-\lambda/\mu}}{(1 + \delta/\mu \coth M/\delta R) H e^{L/\mu R} + (1 - \delta/\mu \coth M/\delta R) e^{-L/\mu R}} \quad (42)$$

$$\psi = \sigma^2 \delta^2 \frac{(\beta \xi' + 1) - e^{-\beta \lambda}}{(\beta \xi' + 1) - \left[\frac{(X-\beta) - (X+\beta)P}{(X+\beta) - (X-\beta)P} \right] e^{-\beta L/R}} \quad (51)$$

$$\psi = \sigma^2 \delta^2 \frac{e^{-(\Omega-\beta)z/2R}}{\frac{P(X-\Omega) - (X+\Omega)}{P(X-\beta) - (X+\beta)}} \quad (54)$$

$$\psi = \sigma_+^2 \delta^2 \frac{T e^{(\Omega-\beta)\lambda/2} + e^{-(\Omega+\beta)\lambda/2}}{\left[\frac{P(X-\Omega) - (X+\Omega)}{P(X-\beta) - (X+\beta)} \right] T e^{(\Omega-\beta)L/2R} + \left[\frac{P(X+\Omega) - (X-\Omega)}{P(X-\beta) - (X+\beta)} \right] e^{-(\Omega+\beta)L/2R}} \quad (60)$$

B. Ions and Electrons

Consider a ternary system of electrons and two different positive ions present within the discharge zone shown in Fig. 1. If it is assumed that

$$c_1^+ \ll c_2^+ \approx c_e + c_e' \quad (108)$$

the mass balance equation for the minor ionic specie can be linearized to give

$$D_a \nabla^2 c_1^+ + \underset{\text{ambipolar diffusion}}{k_i c_e c_m} - \underset{\text{ion-electron recombination}}{k_r c_e' c_1^+} = 0 \quad (109)$$

where c_e and c_e' refer to the concentrations of electrons of different energies. Equation (109) can be put in dimensionless form,

$$\frac{d^2 \eta_+}{d\rho^2} + \frac{1}{\rho} \frac{d\eta_+}{d\rho} + \frac{d^2 \eta_+}{dT^2} - \frac{\eta_+}{\delta_+^2} + \sigma_+^2 = 0 \quad (110)$$

where the dimensionless groups are defined in the Appendix. It should be noted that a transformation of coordinates from Fig. 1 has been made,

$$T = \lambda + \frac{\frac{M}{2} - L}{R} \quad (111)$$

The boundary conditions are

$$\eta_+ = 0 \quad \text{at } T = 0 \text{ and } T = M/2R \text{ at all } \rho \quad (112)$$

$$\eta_+ = 0 \quad \text{at } \rho = 1 \text{ and all } T \quad (113)$$

$$\frac{d\eta_+}{d\rho} = 0 \quad \text{at } \rho = 0 \text{ and all } T \quad (114)$$

and the solution is

$$\eta_+ = \sigma_+^2 \delta_+^2 \left[1 - \frac{\cosh T/\delta_+}{\cosh M/2\delta_+ R} \right] - \frac{4\sigma_+^2}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n I_0(\beta_n \rho) \cos \alpha_n T}{\beta_n^2 (2n+1) I_0(\beta_n)} \quad (115)$$

Equation (115) can be progressively simplified to

$$I. \quad \eta_+ = \frac{\sigma_+^2}{2} \left[\left(\frac{M}{2R} \right)^2 - T^2 \right] - \frac{4\sigma_+^2 M^2}{R^2 \pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n I_0(\alpha_n \rho) \cos \alpha_n T}{(2n+1)^3 I_0(\alpha_n)} \quad (116)$$

$$\text{II. } \eta_+ = \sigma_+^2 \delta_+^2 \left[1 - \frac{\cosh \tau / \delta_+}{\cosh M / 2\delta_+ R} \right] - \frac{4\sigma_+^2}{\pi} \left[\frac{I_0(\beta_0 \rho) \cos \alpha_0 \tau}{\beta_0^2 I_0(\beta_0)} \right] \quad (117)$$

$$\text{III. } \eta_+ = \frac{\sigma_+^2}{2} \left[\left(\frac{M}{2R} \right)^2 - \tau^2 \right] - \frac{4\sigma_+^2 M^2}{\pi^2 R^2} \left[\frac{I_0(\alpha_0 \rho) \cos \alpha_0 \tau}{I_0(\alpha_0)} \right] \quad (118)$$

$$\text{IV. } \eta_+ = \frac{\sigma_+^2 M^2}{8R^2} \quad (119)$$

$$\text{V. } \eta_+ = \sigma_+^2 \delta_+^2 \left[1 - \frac{I_0(\rho / \delta_+)}{I_0(1 / \delta_+)} \right] \quad (120)$$

$$\text{VI. } \eta_+ = \frac{\sigma_+^2}{4} \left[1 - \rho^2 \right] \quad (121)$$

$$\text{VII. } \eta_+ = \sigma_+^2 \delta_+^2 \quad (122)$$

when: I. $1/\delta_+^2 = 0$; II. the first root of Eq. (115) is dominant; III. the first root of Eq. (115) is dominant; IV. $\rho = 0$, $\tau = 0$, and $I_0(\alpha_0)$ is large in Eq. (118); V. $\frac{\partial^2 \eta_+}{\partial \tau^2} = 0$; VI. $\frac{\partial^2 \eta_+}{\partial \tau^2} = 0$ and $1/\delta_+^2 = 0$; and VII. $\rho = 0$ and $I_0(1/\delta_+)$ is large in Eq. (120). Carslaw and Jaeger should be consulted for other solutions to these types of equations.²⁵

An average value for the concentration of the minor ionic specie, $\bar{\eta}_+$, can be obtained by the following integration,

$$\bar{\eta}_+ = \frac{\int_0^{M/2R} \int_0^1 \eta_+ d\rho d\tau}{\int_0^{M/2R} \int_0^1 d\rho d\tau} \quad (123)$$

Unfortunately, the integral $\int_0^1 I_0(\alpha_n \rho) d\rho$ cannot be evaluated explicitly.

III. CONSEQUENCES

A. Previous Results

For the sake of brevity, a number of topics pertaining to the discharge zone given previously will not be repeated here. The reader is referred to the following sub-sections of Sec. VI in reference (19): A. Choice of Steady-State Systems; B. Complexity of Solutions; C. Velocity and Mass Flux; D. Residence Time; E. Radial Concentration Gradients; F. Comparison of Rate Processes; I. Back Diffusion; and M. Surface Reaction vs Atom Production.

B. Measurement of k_0

1. Comparison of Rate Processes

The behavior of atoms in the system shown in Fig. 1 is characterized by eight different rate processes: convection, radial diffusion to the walls,

axial diffusion through the discharge zone, axial diffusion through the reactor zone, production, recombination on the end plate, recombination in the discharge zone, and recombination in the reactor zone. Thus, the interaction between the rate of production and the other rate processes can be conveniently characterized by seven dimensionless groups:

$$\sigma^2 = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of radial diffusion to the wall}} = \frac{k_0' R^2}{D_{12}}$$

$$\frac{\sigma^2}{1/\delta'^2} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of atom recombination within the discharge zone}} = \frac{k_0'}{k_1'} \text{ or } \frac{2k_0' R}{\gamma v_1}$$

$$\frac{\sigma^2}{1/\mu^2} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of atom recombination within the reactor zone}} = \frac{k_0'}{k_1'} \text{ or } \frac{2k_0' R}{\gamma v_1}$$

$$\frac{\sigma^2}{1/\xi'} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of atom recombination on the end plate}} = \frac{4k_0' R}{\gamma' v_1}$$

$$\frac{\sigma^2}{\beta} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of axial convection}} = \frac{k_0' R}{v_z}$$

$$\frac{\sigma^2}{R/M} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of axial diffusion through the discharge zone}} = \frac{k_0' R M}{D_{12}}$$

$$\frac{\sigma^2}{R/L} = \frac{\text{rate of atom production in the discharge zone}}{\text{rate of axial diffusion through the reactor zone}} = \frac{k_0' R L}{D_{12}}$$

These dimensionless groups can be further condensed to yield just two groups relating the overall rates of atom production, transport, and loss:

$$\frac{\phi_{\text{prod}}}{\phi_{\text{loss}}} = \frac{\text{rate of atom production}}{\text{rate of atom loss}} = \frac{\sigma^2}{1/\xi' + 1/\delta'^2 + 1/\mu^2} \quad (124)$$

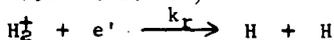
$$\frac{\phi_{\text{loss}}}{\phi_{\text{transport}}} = \frac{\text{rate of atom loss}}{\text{rate of atom transport}} = \frac{1/\xi' + 1/\delta'^2 + 1/\mu^2}{R/L + R/M + \beta + 1} \quad (125)$$

In a steady-state experiment, there must be a competition between two rate processes -- a source and a sink. If the source and sink are spatially separated, then a transport process may further complicate the results. In the present case, the rate of atom production can be measured only if

$\frac{\phi_{\text{prod}}}{\phi_{\text{loss}}} < 1$, for if the source is much greater than the sink, no concentration gradient can exist.

2. Significance of k_0'

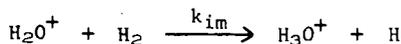
For purposes of discussion, assume that the rate parameter k_0' represents the rate of production of atomic hydrogen (c_1') via the following ion-electron recombination reaction,



Thus,

$$k'_0(c - c_1) = \frac{dc_1}{dt} = 2k_r(H_2^+)(e') \quad (126)$$

defines the parameter k'_0 . If atomic hydrogen is also produced when water is present via an ion-molecule reaction,



k'_0 changes to

$$k'_0(c - c_1) = \frac{dc_1}{dt} = 2k_r(H_2^+)(e') + k_{im}(c - c_1)(H_2O^+) \quad (127)$$

It is clear from the above that k'_0 is a composite parameter which rarely can be subdivided into its component parameters from discharge product measurements alone. Furthermore, as shown in Sec. II. B., the ion and electron concentrations are not uniform throughout the discharge zone, so an average value, \bar{k}'_0 , is observed,

$$\bar{k}'_0(c - c_1) = 2k_r(H_2^+)_{AV}(e')_{AV} + k_{im}(c - c_1)(H_2O^+)_{AV} \quad (128)$$

Thus, the measurement of absolute yields of discharge products is not a fruitful technique for studying discharge-zone kinetics. An exception to this statement occurs when the discharge is initially well characterized and perturbations are made on this initial state. For example, in the absence and presence of water, the ratio of the above rate parameters \bar{k}'_0 becomes

$$\frac{\bar{k}'_0(c - c_1)|_{\text{with } H_2O}}{\bar{k}'_0(c - c_1)|_{\text{no } H_2O}} = 1 + \frac{k_{im}(c - c_1)(H_2O^+)_{AV}}{2k_r(H_2^+)_{AV}(e')_{AV}} \quad (129)$$

The quantity $k_{im}(H_2O^+)_{AV}$ can be determined provided that the ratio of \bar{k}'_0 values is measurable and the other quantities are known.

3. Interaction Between Discharge and Reactor Zones

The activity of the reactor-zone walls and the location of the catalytic end plate have a measurable influence upon the atom concentration within the discharge zone and at the discharge-zone boundary. This phenomenon can be used to advantage for the measurement of absolute or relative values of the rate constant of atom production k'_0 .

In the absence of reactor-zone sinks, Eqs. (27) and (45) apply,

$$\psi = \sigma^2 \delta^2 = \frac{k'_0}{k'_0 + k_1} \quad \text{or} \quad \frac{k'_0}{k'_0 + \frac{\gamma \bar{v}_1}{2R}} \quad (130)$$

The atom production rate constant k'_0 can be determined from Eq. (130) provided that (a) the amount of atom recombination on the discharge-zone walls is known, (b) it remains constant during the measurement process, and (c) it is the dominant atom loss process. In an electrode discharge, metal sputtering on

the tube walls occurs continuously and the above conditions are not fulfilled. With other types of discharges, a period of wall aging may be required.

If an end plate is present, the concentration of atoms at the discharge boundary ($\lambda = L/R$) is given by Eq. (33),

$$\psi = \sigma^2 \delta^2 \frac{\frac{L}{R} + \xi'}{\frac{L}{R} + \xi' + \frac{\delta^2 R}{M}} \quad \left(\frac{M}{\delta R} \leq 1/4 \right) \quad (131)$$

When $L/R + \xi' \gg \frac{\delta^2 R}{M}$, then $\psi = \sigma^2 \delta^2$ as previously. However, if $\frac{\delta^2 R}{M} \gg L/R + \xi'$, then

$$\psi = \frac{M}{R} \sigma^2 \left(\frac{L}{R} + \xi' \right) = \frac{M k_0'}{D_{12}} \left(L + \frac{4D_{12}}{\gamma_1 v_1} \right) \quad (132)$$

The rate constant k_0' can be determined if the recombination coefficient of the end plate or the diffusion coefficient of the atoms is known.

If only the reactor-zone walls are active, Eq. (36) applies at the discharge-zone boundary ($z = 0$),

$$\psi = \sigma^2 \delta^2 \frac{1}{1 + \frac{\delta^2 R}{\mu M}} \quad \left(\frac{M}{\delta R} \leq 1/4 \right) \quad (133)$$

The only new result occurs when $\frac{\delta^2 R}{\mu M} \gg 1$, and leads to

$$\psi = \sigma^2 \frac{M}{R} \mu = k_0' M \left(\frac{2R}{D_{12} \gamma_1 v_1} \right)^{1/2} \quad (134)$$

which is no improvement over Eq. (132). Equations (42), (51), (54), and (60) lead to progressively more complicated solutions.

In the preceding paragraphs we have been preoccupied with the measurement of k_0' . The equations derived above are equally applicable if k_0' is already known and show how such data can be used to predict steady-state atom concentration levels in diffusion and flow tubes.

As an example, consider the effect of an end plate on the atom concentration within the discharge zone. In the absence of the end plate, the concentration throughout the reaction tube is given by Eq. (130). When the end plate is present, either Eq. (33) or Eq. (131) applies for the reactor zone and Eq. (135) applies for the discharge zone (z assumes negative values only between 0 and $-M$).

$$\eta = \sigma^2 \delta^2 \left[1 - \frac{\delta \frac{\cosh \left(\frac{z+M}{\delta R} \right)}{\sinh M/\delta R}}{\frac{L}{R} + \xi' + \delta \coth \frac{M}{\delta R}} \right] \quad (135)$$

With $R = 2$ cm, $D_{12} = 1.25 \cdot 10^4$ cm²/sec (atomic hydrogen at 100 mTorr and 25°C), $L = 10$ cm, $v_1 = 2.5 \cdot 10^5$ cm/sec (atomic hydrogen), $M = 8$ cm, $v_2 = 0$ cm/sec,

$\gamma_{\text{walls}} = 10^{-5}$, $\gamma'_{\text{end plate}} = 10^{-2}$, and $k_0' = 0.100 \text{ sec}^{-1}$, the average atom concentration in the discharge zone is reduced from 14% to 0.19%. It is assumed here that the end plate has no effect on the electron and ion concentration levels within the discharge.

4. Mass-Flux Devices

As shown above, the measurement of the absolute value of k_0' requires a knowledge of either γ , M and D_{12} , or M and γ' . A simpler procedure applicable to the study of atoms requires the use of a mass-flux device such as an isothermal calorimeter, which measures the atom flux at a given point within the reactor zone.¹⁹ Equation (131) becomes

$$\begin{aligned} J_{1s} \text{ (atoms/cm}^2 \text{ sec)} &= - D_{12} \left. \frac{\partial c_1}{\partial z} \right]_{z=L} = \frac{c D_{12}}{R} \left. \frac{\partial \psi}{\partial \lambda} \right]_{\lambda=0} \\ &= \sigma^2 \delta^2 \frac{c D_{12} / R}{\frac{L}{R} + \xi' + \frac{\delta^2 R}{M}} \approx \frac{M}{R} \sigma^2 \frac{c D_{12}}{R} = k_0' M c \end{aligned} \quad (136)$$

when $\frac{\delta^2 R}{M} \gg \left(\frac{L}{R} + \xi' \right)$. Thus, the rate of atom production can be determined by a mass-flux measurement provided that the value of M is known and the calorimeter is the dominant atom sink.

5. Relative Measurements

Provided that certain parameters remain constant and the appropriate inequality relationships hold, the measurement of relative values of k_0' is the easiest measurement to perform in diffusion or flow tubes. The most important requirement is that $\frac{\Phi_{\text{prod}}}{\Phi_{\text{loss}}} \ll 1$, as discussed in Sec. III. B. 1. The desired relationship

$$\psi = \text{constant} \cdot k_0' \quad (137)$$

is rigorously correct for any of the following cases:

- I. $\sigma^2 \delta^2 \ll 1$ in Eq. (130);
- II. $\left(\frac{L}{R} + \xi' \right) \gg \frac{\delta^2 R}{M}$ and $\sigma^2 \delta^2 \ll 1$ in Eq. (131);
- III. $\frac{\delta^2 R}{M} \gg \left(\frac{L}{R} + \xi' \right)$, $M = \text{constant}$, $L = \text{constant}$, and $\xi' = \text{constant}$ in Eq. (131);
- IV. $\frac{\delta^2 R}{\mu M} \ll 1$ and $\sigma^2 \delta^2 \ll 1$ in Eq. (133);
- V. $\frac{\delta^2 R}{\mu M} \gg 1$, $M = \text{constant}$, and $\mu = \text{constant}$ in Eq. (133);
- VI. $\frac{\delta^2 R}{M} \gg \left(\frac{L}{R} + \xi' \right)$ and $M = \text{constant}$ in Eq. (136); and

$$\text{VII. } \left(\frac{L}{R} + \xi' \right) \gg \frac{\delta^2 R}{M}, \quad \sigma^2 \delta^2 \ll 1, \quad L = \text{constant}, \quad \text{and } \xi' = \text{constant in Eq. (136).}$$

The above list is not exhaustive, since any of the solutions in Sec. II. A. can be used if the proper conditions are fulfilled.

6. Multiple Discharge Products

When more than one discharge product is formed, the simplest mass-balance equations and boundary conditions become

$$\frac{d^2 \eta_i}{d\lambda^2} + \sigma_i^2 (1 - \sum_{j=1}^n \eta_j) - \frac{\eta_i}{\delta_i^2} = 0 \quad \text{and} \quad \frac{d^2 \psi_i}{d\lambda^2} = 0 \quad (138)$$

$$\frac{d\eta_i}{d\lambda} = 0 \quad \text{at} \quad \lambda = \infty \quad \text{and} \quad \frac{d\psi_i}{d\lambda} = 0 \quad \text{at} \quad \lambda = -\infty \quad (139)$$

The solution is of the form

$$\psi_i = \eta_i = \sigma_i^2 \delta_i^2 \left[\frac{1 - \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{\sigma_j^2 \delta_j^2}}{\sigma_i^2 \delta_i^2 - \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{\sigma_j^2 \delta_j^2}} \right] \quad (140)$$

which, if the total amount of product is small, simplifies to

$$\psi_i = \eta_i \approx \sigma_i^2 \delta_i^2 \quad (141)$$

If there are no sinks, a discharge product will not disappear once it has been formed. For moderately stable molecules, such sinks include decomposition on the walls of the reaction tube and reaction with other gas-phase components. Conditions can be adjusted to minimize these loss processes, a fact which accounts for the variety of novel chemical species that can be produced from chemical discharge systems.²⁶⁻²⁹

IV. SUMMARY AND CONCLUSIONS

The rate of production of a given chemical intermediate in a diffusion or flow tube is characterized by k_0' , a composite parameter incorporating the rates of ionization, ion-electron recombination, ion-molecule reactions, electron attachment, wall recombination, ion-ion recombination, ambipolar diffusion, and other kinetic processes occurring within the discharge zone. The measurement of the absolute value of k_0' requires a knowledge of either γ , M , M and D_{12} , or M and γ' . Relative measurements of k_0' are possible under a wide variety of conditions. Many novel chemical species can be produced from such systems if all homogeneous and heterogeneous sinks are minimized.

V. NOTATION

∇	Del operator (vector)
∞	Infinity
{ }	Braces indicating molar concentration of enclosed species
c	Total molar concentration of gaseous species
c_1	Molar concentration of atoms in reactor zone
c_1^+	Molar concentration of atoms in discharge zone
c_2^+	Molar concentration of minor positive ionic specie
c_2^-	Molar concentration of major positive ionic specie
c_e	Molar concentration of high-energy electrons
c_e'	Molar concentration of low-energy electrons
D_{12}	Binary diffusion coefficient for atom-molecule system
D_a	Ambipolar diffusion coefficient
e	Exponential
i	Represents quantity related to specie i
$I_0()$	Modified Bessel function
j	Represents quantity related to specie j
J_{1s}	Molar flux of atoms to end plate
k_1	First-order rate constant for loss of atoms in reactor zone
k_1^+	First-order rate constant for loss of atoms in discharge zone
k_0^+	First-order rate constant for production of atoms in discharge zone
\bar{k}_0^+	Averaged first-order rate constant k_0^+
k_i	Second-order ionization rate constant
k_r	Second-order ion-electron recombination rate constant
k_{im}	Second-order ion-molecule reaction rate constant
L	Length of reactor zone to end plate
M	Length of discharge zone (or half the length for a symmetrical system)
R	Radius of reaction tube
v_z	Mass-average velocity in z direction (axial direction)
$\frac{v_z}{v_1}$	Velocity of an atom
z	Distance from discharge-reactor zone boundary to end plate (+ direction)

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APPENDIX

$$\lambda = \frac{L - z}{R}$$

$$T = \lambda + \frac{M/2 - L}{R}$$

$$\rho = \frac{r}{R}$$

$$\psi = \frac{c_1}{c}$$

$$\eta = \frac{c_1'}{c}$$

$$\beta = \frac{v_2 R}{D_{12}}$$

$$\sigma^2 = \frac{k_0' R^2}{D_{12}}$$

$$\delta_{s,2} = \frac{2D_{12}(1 - \gamma/2)}{R\gamma\bar{v}_1} \quad (\text{surface phase})$$

$$\delta_{g,2} = \frac{D_{12}}{k_1' R^2} \quad (\text{gas phase})$$

$$\mu^2 = \frac{2D_{12}(1 - \gamma/2)}{R\gamma\bar{v}_1} \quad (\text{surface phase})$$

$$\mu^2 = \frac{D_{12}}{k_1' R^2} \quad (\text{gas phase})$$

$$\eta_+ = \frac{c_1^+}{c}$$

$$\bar{\eta}_+ = \frac{c_1^+}{c}$$

$$\xi_1' = \frac{4D_{12}(1 - \gamma'/2)}{R\gamma'\bar{v}_1}$$

$$\gamma = \frac{2k_1 R}{\bar{v}_1}$$

$$\frac{1}{\delta^2} = \sigma^2 + \frac{1}{\delta_{s,2}^2}$$

$$\frac{\Omega}{2} = \left[\frac{\beta^2}{4} + \frac{1}{\mu^2} \right]^{\frac{1}{2}}$$

$$\frac{X}{2} = \left[\frac{\beta^2}{4} + \frac{1}{\delta^2} \right]^{\frac{1}{2}}$$

$$H = \frac{\xi_1' + \mu}{\xi_1' - \mu}$$

$$P = \left(\frac{X + \beta}{X - \beta} \right) e^{-MX/R}$$

$$T = \frac{\Omega\xi_1' + \beta\xi_1' + 2}{\Omega\xi_1' - \beta\xi_1' - 2}$$

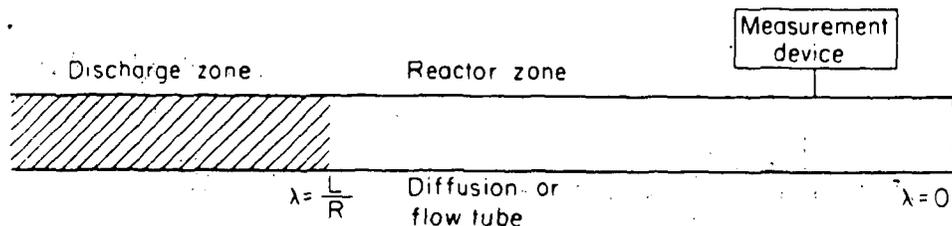
$$\sigma_+^2 = \frac{k_1 c_e R^2}{D_a}$$

$$\delta_{+,2} = \frac{k_r c_e' R^2}{D_a}$$

$$\alpha_n = \frac{\pi R(2n + 1)}{M}$$

$$\beta_n^2 = \alpha_n^2 + \frac{1}{\delta_{+,2}^2}$$

$$\frac{1}{\delta_{i,1}^2} = \sigma_{i,1}^2 + \frac{1}{\delta_{i,2}^2}$$



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Fig. 1. Schematic drawing of a typical "reaction tube," showing the location of the discharge zone, the reactor zone, the discharge-zone boundary (at $\lambda = L/R$), and the end plate (at $\lambda = 0$).

Table 1. Rate processes occurring within a typical reaction tube.²⁴

<u>Ions and Electrons in Discharge Zone</u>	<u>Neutral Species in Discharge and Reactor Zones</u>
PRODUCTION: Ionization Photoionization Ion-molecule Reactions Electron Attachment Charge Transfer Metastable Atom Reactions	Ion-electron Recombination Ion-ion Recombination Ion-molecule Reactions Electron Attachment Wall Recombination of Ions
LOSS: Ion-electron Recombination Ion-ion Recombination Wall Recombination Loss to Measurement Device Electron Detachment	Gas-kinetic Reactions Recombination on Walls Recombination on End Plate Loss to Measurement Device
TRANSPORT: Convection Diffusion Ambipolar Diffusion Drift Cyclotron Resonance	Convection Diffusion