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Diffusion and Heterogeneous Reaction. VI. Surface Recombination in the Presence of Distributed Atom Sources*

HENRY WISE, CLARENCE M. ABLOW, AND KENNETH M. SANCIER

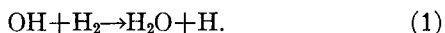
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A theoretical analysis is made of the simultaneous removal of atoms by a first-order heterogeneous reaction and their generation by a second-order gas-phase reaction. Such a model is found applicable to a system in which hydrogen atoms recombine on the walls of a cylindrical vessel in the presence of hydroxyl radicals which may interact in the gas by reaction with hydrogen molecules. The perturbation of the hydrogen-atom-concentration profile in the cylinder due to OH as measured by electron spin resonance spectroscopy is employed to calculate the rate constant for the gas-phase reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$.

INTRODUCTION

THE generation of atomic hydrogen by means of electrical discharges through molecular hydrogen has been the subject of a number of publications.¹⁻³ Of special interest has been the role of water vapor in the production and decay of the hydrogen atoms as a result of homogeneous and heterogeneous reactions.^{4,5} Generally it has been assumed that the increased lifetime of hydrogen atoms in the presence of water vapor is due to poisoning of the glass for atom recombination. However, recent measurements have indicated that water vapor does not affect the catalytic efficiency of Pyrex glass for hydrogen atoms^{5,6} or oxygen atoms.⁷ It may be concluded therefore that the marked influence of water vapor on the decay rate of hydrogen atoms is associated with the production of such atoms by further reaction of some of the products issuing from a discharge through moist hydrogen, especially



The kinetics of this reaction has been investigated under different experimental conditions,⁸⁻¹² and results reported have shown disagreement as discussed in some detail in Ref. 8.

In our experimental program on the surface-catalyzed kinetics of atom recombination we examined the decay of hydrogen atoms in a cylindrical glass tube and the influence of OH radicals on the hydrogen-atom-concentration profile. From such measurements carried out with the aid of an electron spin resonance (ESR) spectrometer the rate constant for Reaction (1) could be evaluated. In the interpretation of the ESR data a theoretical analysis was required which took into account the diffusive flow of hydrogen atoms and hydroxyl radicals in the presence of distributed sources of hydrogen atoms due to Reaction (1).

THEORETICAL ANALYSIS

In the mathematical model we consider the reactive species H and OH, which disappear by heterogeneous reaction on the walls of a cylindrical tube of infinite length, and a gas-phase reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ which leads to the formation of H atoms.¹³ The particle density of hydrogen atoms is given by n , that of hydroxyl radicals by m , and that of hydrogen molecules by M . For diffusive flow in a cylinder the steady-state balance of the number of active particles entering and leaving an arbitrary volume leads to

$$D_{12}\Delta n + kmM = 0, \quad (2)$$

$$D_{32}\Delta m - kmM = 0, \quad (3)$$

where D_{12} and D_{32} represent the binary diffusion coefficients of H in H_2 and OH in H_2 , k , the rate constant for Reaction (1), and Δ , the Laplacian operator. It is assumed that the concentration of H(n) and OH(m) are small relative to that of H_2 (M) so that M remains essentially constant over the entire length of the tube. Also all coefficients appearing in Eqs. (2) and (3) are taken to be constants.

¹³ The contribution of other chemical reactions involving OH is discussed in the last section.

* This work was sponsored by Project Squid, which is supported by the Office of Naval Research, Department of the Navy.

¹ H. G. Poole, Proc. Roy. Soc. (London) **A163**, 404, 415, 424 (1937).

² T. M. Shaw, J. Chem. Phys. **30**, 1366 (1959).

³ S. J. B. Corrigan and A. von Engel, Proc. Roy. Soc. (London) **A245**, 335 (1958).

⁴ T. M. Shaw, J. Chem. Phys. **31**, 1142 (1959).

⁵ F. D. Coffin, J. Chem. Phys. **30**, 593 (1959).

⁶ H. Wise and W. A. Rosser, Symp. Combust. 9th, Cornell Univ., Ithaca, N. Y. 738 (1963).

⁷ J. C. Greaves and J. W. Linnett, Trans. Faraday Soc. **55**, 1346 (1959).

⁸ F. Kaufman and F. P. Del Greco, Ref. 6, p. 659.

⁹ F. P. Del Greco and F. Kaufman, Discussions Faraday Soc. **33**, 128 (1962).

¹⁰ L. J. Avramenko and R. V. Lorentso, Zh. Fiz. Khim. **24**, 207 (1950).

¹¹ C. P. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 993 (1961).

¹² R. T. Baldwin, Trans. Faraday Soc. **52**, 1344 (1956).

The catalytic activities of the cylinder wall (at $r=R$) are expressed by the boundary conditions:

$$\partial n / \partial r(R, x) = -n(R, x) / \delta_1 R, \quad (4)$$

$$\partial m / \partial r(R, x) = -m(R, x) / \delta_3 R, \quad (5)$$

where δ_1 and δ_3 are dimensionless numbers¹⁴ related to the surface-catalytic recombination coefficients γ_1 and γ_3 for H and OH,

$$\delta_a = 4D_{a2}[1 - (\gamma_a/2)]\gamma_a c_a R, \quad (6)$$

where c_a is the mean velocity of atom or radical, D_{a2} the appropriate binary diffusion coefficient, and the subscript a is 1 for H and 3 for OH. At the source ($x=0$) the density of active species has a uniform value:

$$n(r, 0) = n_0, \quad (7)$$

$$m(r, 0) = m_0. \quad (8)$$

Also because of symmetry the radial density gradient vanishes at the axis of the cylinder:

$$(\partial n / \partial r)(0, x) = \partial m / \partial r(0, x) = 0. \quad (9)$$

For an infinite tube the concentration of active species tends to zero away from the source:

$$n(r, \infty) = m(r, \infty) = 0. \quad (10)$$

The solution of the differential equations satisfying these boundary conditions is described in Appendix A. At a distance x from the source one obtains for the density of active species averaged over the cross section of the tube:

$$\bar{m} = 2m_0 \sum_{i=1}^{\infty} \frac{A_i J_1(\alpha_i)}{\alpha_i} \exp\left(-\frac{\beta_i x}{R}\right), \quad (11)$$

$$\bar{n} = -\frac{D_{32}}{D_{12}} \bar{m} + 2m_0 \sum_{i=1}^{\infty} \frac{C_i J_1(\beta_i)}{\beta_i} e^{-\beta_i x/R} + 2n_0 \sum_{i=1}^{\infty} E_i \frac{J_1(\epsilon_i)}{\epsilon_i} e^{-\epsilon_i x/R}, \quad (12)$$

where α_i ($i=1, 2, 3, \dots$) are the roots of the equation $J_0(\alpha_i) = \alpha_i \delta_1 J_1(\alpha_i)$ with J_0 and J_1 Bessel functions of orders zero and one; β_i is defined as

$$\beta_i = [\alpha_i^2 + (kMR^2/D_{32})]^{\frac{1}{2}},$$

and ϵ_i as the roots of the equation $J_0(\epsilon_i) = \epsilon_i \delta_3 J_1(\epsilon_i)$. A_i , C_i , and E_i are constants determined by the boundary conditions (cf. Appendix A).

A number of approximations may be introduced which are applicable to the problem under consideration. For low catalytic activity of the cylinder walls, i.e., $\delta_1 \gg 1$, $\delta_3 \gg 1$, and the term $\beta_1 \doteq (kMR^2/D_{32})^{\frac{1}{2}} \ll 1$ the average concentration of atoms at a cross section is

¹⁴ H. Motz and H. Wise, J. Chem. Phys. **32**, 1893 (1960).

given by

$$(\bar{n}/n_0) e^{\epsilon_1 x/R} = (1-\sigma) + \sigma e^{(\epsilon_1 - \beta_1)x/R}, \quad (13)$$

where

$$\sigma = \frac{m_0}{n_0} \frac{D_{32}}{D_{12}} \frac{\delta_1}{\delta_3} \left(\frac{\beta_1^2 \delta_3}{2} - 1 \right). \quad (14)$$

EXPERIMENTAL MEASUREMENTS

The experimental apparatus employed in the measurement of hydrogen-atom density was similar to that described in Ref. (15). The hydrogen atoms, produced by means of an electrodeless discharge (14 Mc/sec), were allowed to diffuse in a quartz cylinder (0.76 cm i.d., 60 cm long) closed at one end. A larger quartz tube (3.5 cm i.d., 70 cm long) was joined to the cylinder in the form of a T tube, which in turn was connected to the rest of the vacuum system. The diffusion tube was cleaned with nitric acid (10M) and thoroughly rinsed with distilled water. Hydrogen gas (Matheson, commercial grade) at a pressure of about 1000 Torr after passage through a De-Oxo unit was saturated with water vapor by means of a water bubbler maintained at about 20°C. The pressure in the vacuum system was established by adjusting the hydrogen flow through a leak valve (Granville-Phillips). Traps cooled in liquid nitrogen were placed on the upstream side of the McLeod gauge and of the pumping assembly composed of mechanical and diffusion pumps.

The hydrogen-atom concentration within the diffusion tube resulting from homogeneous and heterogeneous reactions was determined by moving the ESR cavity-magnet assembly mounted on a wheeled carriage to various positions along the tube. By this means the longitudinal atom-concentration profile could be obtained integrated over the cross section of the tube and the effective width of the cavity (Table I).

The electrodeless discharge appeared to be affected by the proximity of the ESR magnet. In order to reduce such variations in atom density at the source, a tung-

TABLE I. Relative hydrogen-atom concentration as a function of distance.

x/R	\bar{n}/n_0	
	0.11 Torr ^a	0.15 Torr ^a
0	1.00	1.00
9	0.80	0.86
20	0.56	0.74
30	0.45	0.69
40	0.35	0.60
50	0.27	0.52
60	0.20	0.45

^a Total gas pressure.

¹⁵ B. J. Wood, J. S. Mills, and H. Wise, J. Phys. Chem. **67**, 1462 (1963).

sten-filament calorimeter¹⁶ was employed to monitor the hydrogen atom density at the entrance to the diffusion tube. The presence of other species does not appear to affect the response of the heated metal filament to hydrogen atoms.¹⁷ A constant atom density was produced by suitable adjustment of the discharge power supply in accordance with the response of the calorimeter. The ESR cavity was modified by removing one of its stacks, in order to reduce to 3.4 cm the distance of approach between the center of the cavity and the entrance to the diffusion tube. The ESR cavity (Varian V-4531) was operated at a microwave frequency of about 9.4 kMc/sec and with 100-kc/sec field modulation. For absolute atom density measurements the microwave power was attenuated (low-power bridge) to avoid power saturation.

The ESR spectra of the discharged gas exhibited lines chiefly characteristic of hydrogen atoms and molecular oxygen. The absolute hydrogen-atom density was determined by using molecular oxygen as a standard of spin density^{15,18}; for this purpose the molecular oxygen transition $K=1$, $J=2$, $M=1 \rightarrow 2$ was used.¹⁹ Near the mouth of the diffusion tube it is estimated that about 5% of the molecular hydrogen was dissociated at the two pressures studied. The OH-radical density was not determined since signals due to the electric-dipole transitions²⁰ of the hydroxyl radicals could not be observed in our cavity.

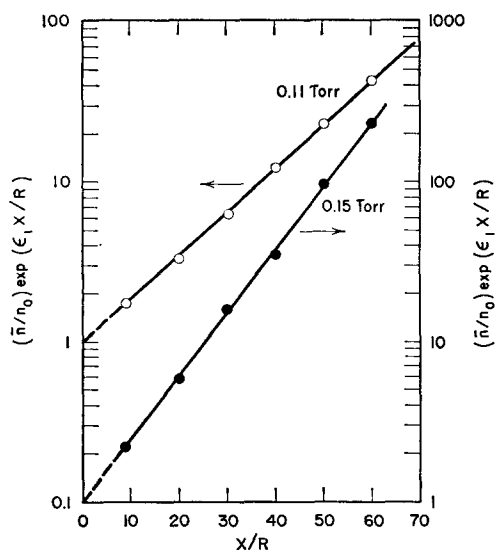


FIG. 1. Relative hydrogen-atom concentration resulting from heterogeneous and homogeneous reactions.

¹⁶ B. J. Wood and H. Wise, *J. Phys. Chem.* **65**, 1976 (1961).

¹⁷ D. Schott and H. Wise (unpublished data).

¹⁸ A. A. Westenberg and N. de Haas, *J. Chem. Phys.* **40**, 3087 (1964).

¹⁹ M. Tinkham and N. W. P. Strandberg, *Phys. Rev.* **97**, 937 (1955).

²⁰ H. E. Radford, *Phys. Rev.* **122**, 114 (1961).

TABLE II. Rate constant for $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ (Temp. 300°K).

Pressure (Torr)	$\epsilon_1 - \beta_1$ $\times 10^2$	ϵ_1 $\times 10^2$	k/D_{32} $\times 10^6$	[(mole/cc) ⁻¹ sec ⁻¹] $\times 10^{-9}$	
				k_a^a	k_b^b
0.11	6.8	10.5	14.5	7.1	9.1
0.15	9.1	12.3	8.0	2.9	3.7
				Av. 5.0	Av. 6.4

^a Based on a value²¹ of $D_{32}P = 5.4 \times 10^3 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$.

^b Based on a value²² of $D_{32}P = 6.9 \times 10^3 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$.

EXPERIMENTAL RESULTS AND DISCUSSION

The functional form of Eq. (13) suggests a graphical procedure for evaluation of the term β_1 containing the rate constant for Reaction (1) from measurements of the change in hydrogen-atom concentration n with distance x/R . Such an analysis was applied to the experimental results presented in Table I. It is to be expected that for large values of x/R the first term $(1-\sigma)$ in Eq. (13) will be small relative to the exponential term so that a plot of $\ln[(\bar{n}/n_0) \exp(\epsilon_1 x/R)]$ versus x/R should yield a straight line whose slope is proportional to $(\epsilon_1 - \beta_1)$. The experimental results obtained at two different pressures are plotted in Fig. 1. From the slopes of the lines shown, the rate constant has been computed as summarized in Table II. Since the diffusion coefficient of OH through H_2 (D_{32}) is not well established, two values are given for the rate constant. The first, k_a , is based on OH diffusing through He ,²¹ while the second, k_b , uses an estimated diffusion coefficient of OH through H_2 .²²

The value of ϵ_1 is obtained from previously reported measurements²³ of the recombination coefficient of atomic hydrogen on quartz ($\gamma = 2.8 \times 10^{-3}$). It should be noted that in the evaluation of the rate constant k from Eq. (13) the assumption has been made that the catalytic activity of quartz for the removal of hydroxyl radicals is quite low. From our data we estimate a recombination coefficient $\gamma_{\text{OH}} \approx 5 \times 10^{-6}$, corresponding to a $\delta_3 \geq 2 \times 10^5$ in the pressure range of interest. Similar low activity of glass for OH has been reported by Smith.²⁴

The fact that the data presented in Fig. 1 fall on a straight line over the entire range of measurements suggests that the value of σ in Eq. (13) is approximately unity. This fact is further substantiated by the intercept of the lines. From $\sigma \approx 1$ an estimate may be made of the concentration of hydroxyl radicals relative to hydrogen atoms in our reaction system. By proper substitution into Eq. (14) it is found that

²¹ A. A. Westenberg, *Combust. Flame* **1**, 346 (1957).

²² L. Andrussov, *Z. Elektrochem.* **54**, 556 (1950).

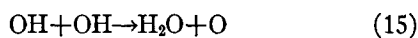
²³ B. J. Wood and H. Wise, *J. Phys. Chem.* **66**, 1049 (1962).

²⁴ W. V. Smith, *J. Chem. Phys.* **11**, 111 (1943).

at the mouth of the diffusion tube the OH concentration is about of the same magnitude as the H concentration, i.e., $m_0 \approx n_0$. An absolute measure of the reactant concentration may be deduced from a first-moment analysis of the electron spin resonance (ESR) signal due to hydrogen atoms and comparison with the ESR signals caused by known concentrations of molecular oxygen as a standard. From such measurements the value of n_0/M is found to be about 0.05; therefore, $m_0/M \approx 0.05$.

It has been reported⁸ that discharges through wet hydrogen are a poor source of OH radicals relative to H atoms. However, under our experimental conditions we were sufficiently far removed from the discharge so that the hydrogen-atom concentration had been materially reduced by wall recombination as compared to the hydroxyl radicals and the relatively poor catalytic properties of glass for the latter species. Also some may have been generated outside the discharge region by reactions involving species containing hydrogen and oxygen.⁹ Therefore the observation that $n_0 \approx m_0$ is not surprising.

In addition it may be concluded from the close fit to a straight line exhibited by the data plotted in Fig. 1 that reactions other than (1) are sufficiently slow as not to affect the decay of H and OH. It is feasible to deduce an estimate of the rate constant for the reaction



by considering the loss of OH to be due to the reactions (1) and (15). Equation (3) would be modified to read

$$D_{32}\Delta m - kmM - 2k_1m^2 = 0, \quad (16)$$

where k refers to the rate constant for Eq. (1), and k_1 for Eq. (15). Because of the low catalytic activity of the glass walls for OH recombination, Eq. (16) becomes one dimensional and may be solved to give

$$\frac{m}{m_0} = \frac{\cosh a - 1}{\cosh[a + x(kM/D_{32})^{1/2}] - 1}, \quad (17)$$

where

$$a = \cosh^{-1}[1 + (3kM/2k_1m_0)]. \quad (18)$$

Since the straight-line behavior of the experimental data (Fig. 1) suggests that where $x/R \geq 10$ Reaction (15) makes a negligible contribution to the decay of OH, we can estimate for the condition $m_0/M = 0.05$ an upper limit to the rate constant, $k_1 \leq 10^{11}$ (mole/cc)⁻¹. This value is in satisfactory agreement with the rate constant quoted in Ref. 25; however, it is somewhat lower than the rate constant obtained by Kaufman and Del Greco.⁸

We estimate an experimental error of about $\pm 20\%$ in the determination of atom densities by electron spin

resonance. In addition, the evaluation of the rate constant k for Reaction (1) is based on the difference between two parameters of similar magnitude ($\epsilon_1 - \beta_1$) and the proportionality $k \propto \beta_1^2$.

On this basis one may readily account for the lack of precision in the computed values of k (Table II). However, the average value for the rate constant compares favorably with that obtained by an entirely different experimental technique employing measurement of the decay in OH concentration in a flowing gas stream.⁸

APPENDIX A

The general solution to Eq. (3) governing the diffusion and gas-phase reaction of the hydroxyl radicals may be found in a way similar to the solution for diffusion alone.²⁶ The solution satisfying boundary conditions given by Eqs. (5), (8), (9), and (10) is

$$m = m_0 \sum_{i=1}^{\infty} A_i e^{-\beta_i x/R} J_0(\alpha_i r/R),$$

where

$$A_i = 2[\alpha_i(1 + \delta_3^2 \alpha_i^2) J_1(\alpha_i)]^{-1},$$

$$\beta_i = [\alpha_i^2 + kMR^2/D_{32}]^{1/2},$$

and α_i is the i th root of $J_0(\alpha_i) = \delta_3 \alpha_i J_1(\alpha_i)$, the J 's being Bessel functions of the first kind. The average concentration of radicals over a cross section is

$$\bar{m} = \frac{2}{R^2} \int_0^R m r dr$$

which expands into the form given in Eq. (11).

If one writes the hydrogen-atom concentration as a sum of two terms,

$$n = q - (D_{32}/D_{12})m,$$

one finds that the reactive term drops out of the diffusion equation to give $\Delta q = 0$. The various boundary conditions on q read

$$\frac{\partial q}{\partial r} = -\frac{q}{\delta_1 R} + \frac{D_{32}}{D_{12}R} \frac{\delta_3 - \delta_1}{\delta_1 \delta_3} m \quad \text{at } r = R,$$

$$q = n_0 + (D_{32}/D_{12})m_0 \quad \text{at } x = 0,$$

$$q = 0 \quad \text{at } x = \infty,$$

$$\partial q / \partial r = 0 \quad \text{at } r = 0.$$

Again, writing q as a sum of a term compatible with the inhomogeneous part of the boundary condition at $r = R$, the part containing m , and another term free of m permits the solution for q to be written as

$$q = m_0 \sum_{i=1}^{\infty} C_i e^{-\beta_i x/R} J_0(\beta_i r/R) + n_0 \sum_{i=1}^{\infty} E_i e^{-\epsilon_i x/R} J_0(\epsilon_i r/R),$$

²⁵ G. L. Schott, J. Chem. Phys. **32**, 710 (1960).

²⁶ H. Wise and C. M. Ablow, J. Chem. Phys. **35**, 10 (1961).

where

$$\epsilon_i \text{ is the } i\text{th root of } J_0(\epsilon_i) = \delta_1 \epsilon_i J_1(\epsilon_i),$$

$$C_i = D_{32} A_i J_0(\alpha_i) (\delta_3 - \delta_1) / D_{12} \delta_3 [J_0(\beta_i) - \beta_i \delta_1 J_1(\beta_i)],$$

$$E_i = \frac{2 \left[\left(1 + \frac{D_{32} m_0}{D_{12} n_0} \right) \epsilon_i J_1(\epsilon_i) - \frac{m_0}{n_0} \sum_{j=1}^{\infty} C_j F_{ji} \right]}{\epsilon_i^2 J_1^2(\epsilon_i) (1 + \delta_1^2 \epsilon_i^2)},$$

$$F_{ji} = [\epsilon_i^2 / (\epsilon_i^2 - \beta_j^2)] [\epsilon_i J_0(\beta_j) J_1(\epsilon_i) - \beta_j J_0(\epsilon_i) J_1(\beta_j)].$$

The average concentration of atoms over a cross section is then found to be as given in Eq. (12).

If the tube wall is relatively inactive for hydroxyl radicals, $\delta_3 \gg 1$ and the α_i are close to roots of J_1 . It follows that A_i , which is approximately equal to $2/\delta_3 \alpha_i^2 J_0(\alpha_i)$, is zero in good approximation for $i=2, 3, 4, \dots$, while $A_1 \approx 1$ since $\alpha_1 \approx (2/\delta_3)^{1/2}$. From this

$$m \approx m_0 e^{-\beta_1 x/R},$$

$$C_i \approx \begin{cases} D_{32} (\delta_3 - \delta_1) / D_{12} \delta_3 [J_0(\beta_1) - \beta_1 \delta_1 J_1(\beta_1)], & i=1 \\ 0, & i=2, 3, \dots, \end{cases}$$

and

$$E_i = \frac{2 \left[\left(1 + \frac{D_{32} m_0}{D_{12} n_0} \right) \epsilon_i J_1(\epsilon_i) - \frac{m_0}{n_0} C_1 F_{1i} \right]}{\epsilon_i^2 J_1^2(\epsilon_i) (1 + \delta_1^2 \epsilon_i^2)}.$$

If the tube wall is also inactive for hydrogen atoms, then $\delta_1 \gg 1$, $\epsilon_i \approx \alpha_i$ ($i=2, 3, 4, \dots$), and $\epsilon_1 \approx (2/\delta_1)^{1/2}$.

This simplifies the expressions above to

$$E_1 = 1 + \frac{D_{32} m_0}{D_{12} n_0} - \frac{m_0}{n_0} C_1 \frac{\epsilon_1^2 J_0(\beta_1) - 2\beta_1 J_1(\beta_1)}{\epsilon_1^2 - \beta_1^2},$$

$$E_i = - (m_0/n_0) C_1 [\epsilon_i^2 J_0(\beta_1) - 2\beta_1 J_1(\beta_1)] / (\epsilon_i^2 - \beta_1^2) J_0(\epsilon_i),$$

$$n = \left[-\frac{D_{32} m_0}{D_{12}} + m_0 C_1 J_0(\beta_1) / R \right] e^{-\beta_1 x/R} + n_0 \sum_{i=1}^{\infty} E_i e^{-\epsilon_i^2 x/R} J_0(\epsilon_i r/R).$$

In averaging n over a tube cross section, all terms of the infinite series after the first drop out, so that

$$\frac{\bar{n}}{n_0} = -\frac{D_{32} m_0}{D_{12} n_0} e^{-\beta_1 x/R} + \frac{m_0}{n_0} C_1 e^{-\beta_1 x/R} \frac{2 J_1(\beta_1)}{\beta_1} + E_1 e^{-\epsilon_1^2 x/R} \frac{2 J_1(\epsilon_1)}{\epsilon_1}.$$

If $\beta_1 \ll 1$ one may simplify further to obtain

$$\bar{n}/n_0 = (1 - \sigma) e^{-\epsilon_1^2 x/R} + \sigma e^{-\beta_1 x/R},$$

where

$$\sigma = (m_0/n_0) (C_1 - D_{32}/D_{12})$$

and

$$C_1 = \frac{D_{32} (1 - \delta_1/\delta_3)}{D_{12} (1 - \beta_1^2 \delta_1/2)}.$$

Finally, $\beta_1^2 \delta_1/2 = \beta_1^2/\epsilon_1^2 \ll 1$; then

$$\sigma = \frac{m_0}{n_0} \frac{D_{32}}{D_{12}} \frac{\delta_1}{\delta_3} \left(\frac{\beta_1^2 \delta_3}{2} - 1 \right).$$

One may note that σ is positive since $\beta_1^2 > \alpha_1^2 = 2/\delta_3$ in the approximations. Also, since $\delta_3 \gg \delta_1$, $\beta_1^2 \delta_1/2$ is much less than 1 as required for the last approximation above.