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ELECTRON-ION AND ION-ION RECOMBINATION COEFFICIENTS FOR USE IN EMP PREDICTION CODES

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A brief survey of some reported electron-ion and ion-ion recombination coefficients is presented. Data which seems most applicable to EMP problems is given along with error estimates, when available.

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SECTION I

INTRODUCTION

A majority of Electromagnetic Pulse (EMP) prediction codes compute an air conductivity by using a lumped-parameter model which is represented by the following equations:

$$\frac{dn_e}{dt} = Q - \beta n_e - \alpha_e n_e n_+ \quad (1)$$

$$\frac{dn_-}{dt} = \beta n_e - \alpha_i n_+ n_- \quad (2)$$

$$n_+ = n_e + n_- \quad (3)$$

where n_e, n_+, and n_- are the secondary electron, positive ion, and negative ion densities; Q is the rate of production of secondary electrons by the source (energy loss by Compton electrons, etc.); β is the attachment rate of electrons to neutrals; α_e is the electron-positive ion recombination coefficient; and α_i is the ion-ion recombination coefficient. The accuracy of a lumped-parameter model appears to be sufficient for most time frames of interest in a relatively undisturbed atmosphere (refs. 1 and 2).

The values of α_e and α_i used in most Air Force Weapons Laboratory (AFWL) EMP codes have not changed significantly for

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1. DNA Reaction Rate Handbook, Edited by M.H. Bortner and T. Baurer, Defense Nuclear Agency, Washington, D.C., DNA 1948H, Revision 6, December 1975.

2. Radasky, W.A., An Examination of the Adequacy of the Three Species Air Chemistry Treatment for the Prediction of Surface Burst EMP, DNA 3880T, Defense Nuclear Agency, Washington, D.C., December 1975.

several years. As calculations are extended to later times, these parameters become more important. This short note surveys some available data for these parameters and suggests values for use in the codes CLASP, SCX, A3D, HEMP-B, FEMP, and HASP. It should be noted that the values given here are not the result of an expert's critical analysis, but of a review of data available to the author which seemed applicable to the problem at hand. Recommended values are given in section 4. This type of data is needed for evaluation of air conductivity uncertainties.

It should be noted that the three-body rate coefficients are given in units of (m^3/s) instead of (m^6/s) because it is the former units which are actually used in equations 1 through 3. These effective three body coefficients are found by multiplying the coefficients in units of m^6/s by the third body density (usually the neutral particle density).

SECTION II

ELECTRON-ION RECOMBINATION

The main electron-ion recombination processes may be divided into the following categories:

1. Two-body
    - a. Dissociative $XY^+ + e \rightarrow X + Y$
    - b. Radiative $X^+ + e \rightarrow X^* + h\nu$
2. Three-body
    - a. Electron-stabilized $X^+ + e + e \rightarrow X^* + e$
    - b. Neutral-stabilized $X^+ + e + M \rightarrow X^* + M$

The two-body processes are independent of altitude (except for constituent variations), while the three-body rates are dependent on the air density and will decrease with increasing altitude. The radiative two-body and electron-stabilized three-body are often collectively referred to as the collisional-radiative recombination process.

1. TWO-BODY

a. Dissociative

Dissociative electron-ion recombination rates from reference 1 are given by table 1. These values are for atmospheric gases and indicate the variations which can be introduced by water vapor, etc. In the section on lumped-parameter computer models of the DNA Reaction Rate Handbook (ref. 1), a value of 3×10^{-13} m^3/s is used for α_{e2}. It is noted that this value is appropriate for moderate to high ionization levels. At lower

Table 1

DISSOCIATIVE ELECTRON-ION RECOMBINATION RATES (Ref. 1)

T = Gas Temperature (K),
T_e= Electron Temperature (K), MKS Units

Rate = $(a \pm \Delta a)(T/300)^{(b\pm\Delta b)}(m^3/s)$

Reactants	a ± Δa	b ± Δb
$N_2^+ + e$	$(2.7\pm.3) \times 10^{-13}$	$-(0.2\pm0.2)\{T\}$
	$(1.8^{+0.4}_{-0.2}) \times 10^{-13}$	$-(0.39)\{T_e\}$
$NO^+ + e$	$(4.1\pm0.3) \times 10^{-13}$	$-(1.0\pm0.2)\{T\}$
	$(4.2\pm0.2) \times 10^{-13}$	$-(0.5\pm0.15)\{T_e\}$
$O^+ + e$	$(2.1\pm0.2) \times 10^{-13}$	$-(0.7\pm0.3)\{T\}$
		$-(0.6\pm0.1)\{T_e\}$
$CO_2^+ + e$	$(3.8\pm0.5) \times 10^{-13}$	$-(0.5\pm?)\{T_e\}$
$H\ CO^+ + e$	$(3.3\pm0.5) \times 10^{-13}$	
	$(2.0\pm0.3) \times 10^{-13}$	$(-0.5\pm?)\{T_e\}$
$N_4^+ + e$	$(2\pm1) \times 10^{-12}$	$(-1\pm?)\{T\}$
$(NO^+ \cdot NO) + e$	$(1.7\pm0.5) \times 10^{-12}$	$-(1\pm?)\{T\}$
$O_4^+ + e$	$(2\pm0.5) \times 10^{-12}$	$-(1\pm?)\{T\}$
$H_3O^+(H_2O)_n$ series ions	$(1-10) \times 10^{-12}$	$-(0.2^{+0.4}_{-0.1})\{T\}$
$NH_4^+(NH_3)_n$ series ions	$(1.3-2.8) \times 10^{-12}$	---

ionization levels the dominant atmospheric ions (below ~80 km) are hydrated ions which have larger rate constants. Radasky (ref. 2) suggested a value of the electron-ion recombination rate at sea level of $2 \times 10^{-13} + 1.3 \times 10^{-11} (f_{H_2O})^{1/3}$ m^3/s where f_{H_2O} is the water vapor fraction ($0.001 \leq f_{H_2O} \leq 0.06$). This value is used in LEMP-2 (ref. 2). This dependence on f (even though the three-body processes dominate at sea level) indicates the importance of certain constituents. Kozlov and Raizer (ref. 4) indicate a range of values for α_e (two-body, dissociative) at 40 to 90 km between 4 and 8×10^{-13} m^3/s, with the most probable values between 5.5 and 8×10^{-13} m^3/s.

There has been some experimental data (ref. 5) which gives a higher estimate of the two-body electron-ion recombination rate, $\sim 10^{-11}$ m^3/s, but the errors in this data taken at 60 to 70 km are uncertain.

The dependence of the two-body recombination coefficient on the electron temperature may be important for EMP calculations.

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3. Longley, H.J., C.L. Longmire, J.S. Malik, R.M. Hamilton, R.N. Marks, and K.S. Smith, Development and Testing of LEMP 2 (U), (Report is Confidential), MRC-R-272, Mission Research Corp., December 1976.

4. Kozlov, S.I., and Y.P. Raizer, "Evaluation of the Coefficient of Dissociative Recombination in the Lower Ionosphere," Cosmic Research, Vol. 4, No. 4, pp. 509-513, 1966.

5. Larsen, T.R., M. Jespersen, et al., "Electron-ion and Ion-ion Reaction Rate Coefficients During a PCA Event," Journal of Atmospheric and Terrestrial Physics, Vol. 34, pp. 787-794, 1972.

Biondi (ref. 6) stated that in most cases this rate is expected to decrease with increasing electron energy. From table 1 and other sources, it is seen that this dependence is roughly $(T_e/300)^{-(0.5\pm0.15)}$. Thus only a factor of three increase in the electron temperature would reduce the two-body rate by almost a factor of two. Since an energy of 1 eV corresponds to a temperature of approximately 1.6×10^4 K, secondary electrons in equilibrium with large electric fields may experience significantly lower recombination rates than those at ambient temperature. From reference 7, the relationship between the electric field and equilibrium electron temperature may be approximated as

$$U_e(\text{eV}) = 0.025e^{(0.583\ell n(10^{-3}E/\text{RAD}))} \qquad (4)$$

where RAD is the relative air density and E is the electric field in volts/meter.

b. Radiative

The rates for radiative recombination are on the order of 4×10^{-18} m^3/s ($O_2^+ + e \rightarrow O_2 + h\nu$) and are small in relation to those for the dissociative processes.

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6. Biondi, M. A., "Studies of the Mechanism of Electron-Ion Recombination, I," Scientific Paper 62-108-511-P1, Westinghouse Research Laboratories, May 4, 1962.

7. Baum, C. E., "Electron Thermalization and Mobility in Air," EMP Theoretical Notes, Note 12, Air Force Weapons Laboratory, July 1965.

2. THREE-BODY

a. Electron-stabilized

When the secondary electron density is large ($\geq 10^{12}$ m^{-3}), capture of an electron by an atomic ion is assisted by a second electron and electron-stabilized recombination results. It appears that the recombination rate for this process is not sensitive to the identity of the singly-charged ions (ref. 1), and available experimental results are consistent with theoretical values. At ∿300 K, the equivalent two-body rate for this process is

$$\alpha_{e_3} \sim 10^{-31} \, n_e \; (m^3/s) \tag{5}$$

where n_e is the secondary electron density in m^{-3}. Thus electron densities must be on the order of 10^{19} m^{-3} in order for this process to be of importance. For electron temperatures $\lesssim 2 \times 10^3$ K, this rate varies with electron temperature approximately as $T_e^{-4.5}$. In most EMP calculations, in regions where the electron density is high enough to make this process important, the electron temperature will be elevated and the significance of this process further reduced.

b. Neutral Stabilized

For neutral-stabilized (three-body) recombination, reference 1 gives a rough estimate of

$$\alpha_{e_3} \; (m^6/s) = 1 \times 10^{-38\pm1} (T/300)^{-(2.5\pm?)} \tag{6}$$

for "air" ions + neutrals + e. Assuming a neutral particle density of $2.547 \times 10^{25}\ m^{-3}$ at sea level (ref. 8), this gives an effective two-body rate

$$\alpha_{e_3}\ (m^3/s) = 2.55 \times 10^{-13\pm1}(T/300)^{-2.5} \tag{7}$$

The rates quoted above as a function of H_2O content are effectively three-body rates with a value of 2×10^{-13} (refs. 2 and 3) for negligible H_2O content. For 3 percent H_2O (∿ saturated air), a value of 4×10^{-12} (refs. 2 and 3) is computed. Baum (ref. 9) quoted a value of

$$\alpha_{e_3}(m^3/s) \simeq 4.5 \times 10^{-12} \tag{8}$$

which has been used in AFWL environment codes for several years. This value is based on experimental work by Van Lint (reported by Baum in ref. 9, based on ref. 10 which presents pressure dependent and temperature dependent data for N_2 and O_2) at atmospheric pressures. Most of the other values are based on work at lower pressures where the formation of complex ions is less likely. It is clearly desirable to have experimental results in air at atmospheric pressure.

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8. U.S. Standard Atmosphere, October 1976.

9. Baum, C.E., "The Calculation of Conduction Electron Parameters in Ionized Air," EMP Theoretical Notes, Note 6, Air Force Weapons Laboratory, March 1965.

10. Van Lint, V.A.J., J. Parez, M.E. Wyatt, D.K. Nichols, Recombination and Attachment in Ionized Gases, RTD TDR-63-3076, Air Force Weapons Laboratory, Kirtland AFB, New Mexico, December 1963.

SECTION III

ION-ION RECOMBINATION

As with electron-ion recombination, there are both two- and three-body processes which need to be considered:

Two-body mutual neutralization $(X^+ + Y^- \rightarrow X + Y)$

and

Three-body (neutral-stabilized) $(X^+ + Y^- + M \rightarrow X + Y + M)$.

1. TWO-BODY MUTUAL NEUTRALIZATION

The DNA Reaction Rate Handbook (ref. 1) gives rate values for this process in the range

$$\alpha_{i_2}(m^3/s) \simeq (0.3\text{-}8) \times 10^{-13}(T/300)^{-0.45\pm0.5} \qquad (9)$$

The value of 3×10^{-14} m^3/s is used in lumped-parameter models discussed in reference 1. As noted in section II, this value is appropriate for moderate to high ionization levels since at lower ionization levels the hydrated ions which have larger rate constants will often dominate (below 80 km). Larsen and Jespersen (ref. 5) estimated a value of $\sim 10^{-13}$ m^3/s from experimental data taken at ∼65 km. Kozlov and Raizer (ref. 4) used a value of 3×10^{-14} m^3/s at high altitudes which would correspond to the two-body process.

A recent review by Smith and Church (ref. 11), which included some of their experimental results, gave a value of

$$\alpha_{i_2}(m^3/s) \simeq 6.8 \times 10^{-13}\ T^{-0.4} \qquad (10)$$

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11. Smith, D., and M.J. Church, "Ion-Ion Recombination Rates in the Earth's Atmosphere," Planetary and Space Science, Vol. 25, pp. 433-439, 1977.

Their values of α_{i_2} as a function of altitude, including temperature effects, are given by table 2. The data of Smith and Church do not seem inconsistent with the other values quoted.

2. THREE-BODY (NEUTRAL STABILIZED)

The rate for this process, also called Thomson recombination, has been given in reference 1 for "air" ions.

$$\alpha_{i_3}(m^6/s) = (3\pm1) \times 10^{-37} \, (T/300)^{-(2.5\pm?)} \tag{11}$$

Work reported in reference 1 measured α_{i_3} in air over the pressure range 0.1 to 1.0 atmosphere and showed a linear dependence of α_{i_3} on neutral gas density as predicted by Thomson's theory. The ions involved were not identified, however. A value of α_{i_3} used in a lumped-parameter model reported in reference 1 is 4.3×10^{-12} m^3/s at sea level.

Reference 2 gives a value of α_i at sea level (three-body dominated) of 1.69×10^{-12} m^3/s. Use of this value provided good agreement with a multi-species air chemistry code. LEMP-2 (ref. 3) uses a value at sea level of 2.1×10^{-12} m^3/s and CLASP (ref. 12) a value of 2.3×10^{-12} m^3/s.

Smith and Church (ref. 11) concluded from their work and previous reviews that, at 300 K,

$$\alpha_{i_3} \, (m^6/s) \sim 2 \times 10^{-37} \tag{12}$$

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12. Jones, C.W., Close-In, Low-Altitude, Self-Consistent Pulse, AFWL TR-75-94, Air Force Weapons Laboratory, June 1976.

Table 2

ION-ION RECOMBINATION COEFFICIENTS (Ref. 11)

Altitude (km)	T (K)	Density (kg/m^3)	α_{i_2} (m^3/s)	Effective α_{i_3} (m^3/s)	α_{i_3}/RAD (see text)
0	288.2	1.225×10^{0}	5×10^{-14}	3×10^{-12}	3×10^{-12}
10	223.2	4.14×10^{-1}		3.5×10^{-12}	1.036×10^{-11}
20	216.7	8.89×10^{-2}		7.5×10^{-13}	1.033×10^{-11}
30	230.7	1.77×10^{-2}	5×10^{-14}	1.5×10^{-13}	1.038×10^{-11}
40	255.3	3.97×10^{-3}		2.5×10^{-14}	7.71×10^{-12}
50	271.6	1.06×10^{-3}		2×10^{-15}	2.3×10^{-12}
60	249.3	3.21×10^{-4}			
70	216.2	8.77×10^{-5}	6.5×10^{-14}		
80	195.0	1.91×10^{-5}			
90	183.8	3.40×10^{-6}	9×10^{-14}		

and that this number is probably accurate to better than a factor of two and is assumed to be independent of the positive and negative ion types and masses. The temperature dependence of this three-body rate is expected to be $T^{-2.5}$ to T^{-3} theoretically, although there is some experimental data which suggests a T^{-4} dependence. Thus, at the lower temperatures in the stratosphere and troposphere it is expected that α_{i_3} will increase, possibly by as much as a factor of two. Values of α_{i_3} in table 2 take this variation into account.

Smith and Church also noted that at pressures approaching one atmosphere, there is evidence from laboratory experiments that recombination rates begin to saturate and eventually decrease with a further increase in pressure. This is contrary to results reported in reference 1 and is due to the onset of Langevin recombination (ref. 13) in which the recombination rate becomes limited by the rate at which ions can drift together under the Coulomb force, i.e., mobility or "diffusion" limited. This effect is included in the values of table 2. The value of α_{i_3} given at sea level is effectively equivalent to the upper limit for two-body ionic recombination coefficients, i.e., that appropriate when every Coulomb collision is stabilized resulting in neutralization.

The values of α_{i_3} given by table 2 are scaled to the same density (sea level) by dividing by the relative air density

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13. Mahan, B.H., Advances in Chemical Physics, (editors, I. Prigogine and S.A. Rice), Vol. 23, Wiley, New York, 1973.

(last column of table 2). These values show the limit due to Langevin recombination at low altitudes and the decrease in recombination at high altitudes. These variations are those that would be seen for α_{i_3} in units of m^6/s (see section I).

Associative ion-ion recombination

$$X^+ + Y^- + N \rightarrow XY + N \tag{13}$$

appears to have a much smaller rate coefficient at ∿300 K than Thomson recombination (ref. 1) and will be ignored.

SECTION IV

SUMMARY

Listed below are electron-ion and ion-ion recombination rates which, based on the sources reviewed, seem to be most appropriate for use in EMP calculations. Rough estimates of the errors involved are also given. (T = gas temperature, T_e = electron temperature.)

1. ELECTRON-ION RECOMBINATION

$$\alpha_e = \alpha_{e_2} + \alpha_{e_3} \tag{14}$$

a. Two-body

$$\alpha_{e_2}(m^3/s) \simeq (7^{+5}_{-3}) \times 10^{-13}(T/300)^{-(0.8\pm0.4)}(T_e/300)^{-0.5\pm0.15} \tag{15}$$

$$T_e \simeq 290\ \mathrm{EXP}(0.583\ \ell n(10^{-3}\ E/\mathrm{RAD}))$$

b. Three-body (ref. 2)

$$\alpha_{e_3}(m^3/s) \simeq [2 \times 10^{-13\pm1} + 1.3 \times 10^{-11}(f_{H_2O})^{1/3}]\ \mathrm{RAD} \tag{16}$$

2. ION-ION RECOMBINATION

$$\alpha_i = \alpha_{i_2} + \alpha_{i_3} \tag{17}$$

a. Two-body

$$\alpha_{i_2}(m^3/s) \simeq (5^{+70}_{-1}) \times 10^{-14}\ (0\text{-}50\ \mathrm{km}) \tag{18}$$

b. Three-body

$$\alpha_{i_3}(\mathrm{m}^3/\mathrm{s}) \approx (3^{+4}_{-1}) \times 10^{-12} + (1.48 \cdot \mathrm{RAD}) \times 10^{-12} \qquad 0 < H < 10 \text{ km} \qquad (19)$$

$$\approx 1.03 \times 10^{-11}\ \mathrm{RAD} \qquad 10 \text{ km} < H < 40 \text{ km}$$

Temperature dependences of these parameters may be of special importance for close-in observers that experience significant temperature increases as the fireball/shockwave effects pass their location. Constituent changes at late times related to radiation/temperature/pressure induced effects may also be of importance. Values of these coefficients as a function of altitude are given by table 3.

As noted in the introduction, these parameter values are not the result of expert analysis, but of a review of available data. It is hoped that the information in this note can serve as a starting point for future reviews of these parameter values. The error estimates can be used as bounds for parametric studies of the importance of these parameter variations in EMP calculations and should be checked against future theoretical and experimental values reported for these rates.

Table 3

RATE COEFFICIENTS

Altitude	RAD	$T=T_e$	α_{e_2}	α_{e_3}*	α_e	α_{i_2}	α_{i_3}	α_i
(km)		K	(m^3/s)	(m^3/s)	(m^3/s)	(m^3/s)	(m^3/s)	(m^3/s)
0	1.0	288	7.4×10^{-13}	2×10^{-13}	9.4×10^{-13}	5×10^{-14}	3×10^{-12}	3×10^{-12}
10	0.34	223	7.4×10^{-13}	6.8×10^{-14}	8.1×10^{-13}	5×10^{-14}	3.5×10^{-12}	3.5×10^{-12}
20	7.26×10^{-2}	217	7.4×10^{-13}	1.45×10^{-14}	7.5×10^{-13}	5×10^{-14}	7.5×10^{-13}	8×10^{-13}
30	1.44×10^{-2}	231	7.4×10^{-13}	2.88×10^{-15}	7.4×10^{-13}	5×10^{-14}	1.5×10^{-13}	2×10^{-13}
40	3.24×10^{-3}	255	7.4×10^{-13}	6.5×10^{-16}	7.4×10^{-13}	5×10^{-14}	3.3×10^{-14}	8.3×10^{-14}

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*$f_{H_2O} = 0$, higher values if $f_{H_2O} > 0$.

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1. DNA Reaction Rate Handbook, Edited by M.H. Bortner and T. Baurer, Defense Nuclear Agency, Washington, D.C., DNA 1948H, Revision 6, December 1975.

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