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A REVIEW OF DATA FOR ELECTRON MOBILITY, ENERGY, AND ATTACHMENT RELEVANT TO EMP AIR CHEMISTRY

M. K. Grover
F. R. Gilmore
R & D Associates
P.O. Box 9695
Marina del Rey, California 90291

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Data and theory are reviewed for EMP air chemistry. It is found that elec- tron energy in moist air subjected to an electric field is very uncertain; that unexplained anomalies exist in the attachment data, especially as a function of pressure; and that the effectiveness of water vapor as a third body for attachment of nonthermal electrons can only be inferred at present from a combined use of theory and data. However, existing EMP air chemistry models are found to predict values of attachment and mobility which generally lie within $\pm 40\%$ of the best present estimates.		

SUMMARY

This report reviews the data for electron mobility, mean electron energy and electron attachment rate in moist air, for electric fields up to about 10^5 V/m·atm, corresponding to mean electron energies up to about 0.5 eV. It is found that recent mobility measurements and calculations based on published rate coefficients generally agree within about 20%. The percentage variations in the mean electron energies derived from various sources are larger, especially for moist air. However, in EMP problems the electron energy enters only as it influences the mobility or the attachment rate, which fact tends to reduce the effects of such uncertainties. The electron attachment rates calculated from various sets of data and also those measured very recently by Price and van Lint near 1 atm show a variety of discrepancies, but all results generally lie within $\pm 40\%$ of a mean curve. The data of McCorkle et al., and to some extent the data of van Lint and Price, suggest that at nitrogen partial pressures above about 0.3 atm the variation of attachment rate with electron energy changes somewhat from that observed at lower nitrogen pressures; however, the anomalies observed are neither well established nor understood at this time.

The mobilities and attachment rates used in existing EMP codes generally lie within the uncertainty ranges of the best current data.

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SECTION 1. ELECTRON MOBILITY AND ELECTRON ENERGY

The electron mobility may be expressed as [1]

$$\mu_e = \frac{4\pi}{3} \frac{|e|}{m} \int_0^{\infty} dv \frac{v^3}{v_m(v)} \frac{\partial f(v)}{\partial v} \equiv \frac{|e|}{m\bar{v}_m} \quad (1)$$

where e and m are the electron charge and mass, $f(v)$ is the distribution function of electron speeds, and $v_m(v)$ is the electron momentum exchange frequency. In a gaseous mixture we may write

$$v_m(v) = \sum_{i=1}^I N_i v_{mi}(v)$$

where N_i is the concentration of species i ($i=1,2,\dots,I$), and $v_{mi}(v)$ is the specific momentum exchange frequency, per molecule, for electrons of speed v interacting with molecular species i . For application to nuclear EMP, the species of interest include nitrogen, oxygen and water vapor.

As far as we are aware, the most recent and comprehensive review of the experimental data for the relevant momentum exchange frequencies is that published by Phelps [2] in the DNA Reaction Rate Handbook. Since the EMP air chemistry models of Baum [3] and of Longley and Longmire [4] have also been based to a substantial degree upon earlier data summaries by Phelps, it is of interest to compare these models with Phelps' more recent compilation, and also to compare Phelps' estimates with some even newer data obtained by Milloy et al. [5], by Rees [6], and by van Lint and Price [7].

For simplicity, the EMP models ignore certain details of the electron distribution function. For example, it is implicitly

assumed that the functional form of the distribution is either invariant or at most a function of the mean electron energy only, under all conditions of interest. In addition, a variety of simplifying approximations are made in the handling of averaged quantities, such as the averaged momentum exchange frequency appearing in the mobility equation. Although the calculation of correct non-Maxwellian distributions and their consistent use for calculating averaged quantities may not yet be fully practicable within the context of the EMP air chemistry model, some thought must still be given to the probable errors resulting from such approximations.

For example, the EMP models assume that the electron mobility in a mixed gas may be calculated as

$$\mu_e^{-1} = \frac{m}{|e|} \sum_{i=1}^I N_i \bar{\nu}_{mi}$$

where the averaged momentum exchange frequencies have been correctly calculated only for the pure Maxwellian gas. To illustrate the type of small but nonnegligible error involved, we have plotted in Figure 1 the mobility of thermal electrons in moist air, as obtained from this approximation, and as obtained from the correct averaging process. It may be seen that the two mobility curves differ by up to ~25%.

Within the context of such approximations, the average electron energy, $\bar{\epsilon}$, may be calculated as

$$\left(\bar{\epsilon} - \frac{3}{2} kT_{\text{gas}} \right) \sum_{i=1}^I N_i \bar{\nu}_{\epsilon i} = e\mu_e E^2 \quad (2)$$

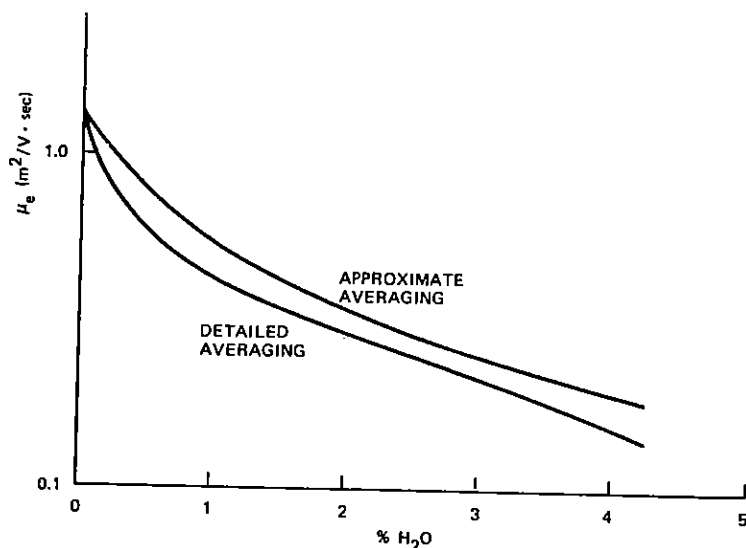


Figure 1. Comparison of Mobility Calculations for Thermal (0.03 eV) Electrons in Moist Air, Calculated Using the Data Compilation of Phelps

where $\bar{\nu}_{ei}$ is now an appropriately averaged energy exchange frequency for electrons of average energy $\bar{\epsilon}$ interacting with molecular species i . Phelps' data compilation [2] also provides estimates of averaged energy exchange frequencies for electrons with nitrogen, oxygen and water vapor molecules.

In Figure 2 we have compared the electron energy calculated from Equations 1 and 2 using Phelps' data compilation with the values of electron energy given by the EMP models of Baum, and Longley and Longmire. The "characteristic electron energy" used in this and later plots is defined to be kT_e , or two-thirds the average electron energy. The plots are for 273°K gas temperature and are for dry air and air with 2% moisture content. The indicated uncertainty ranges are roughly estimated, at only one electron energy,

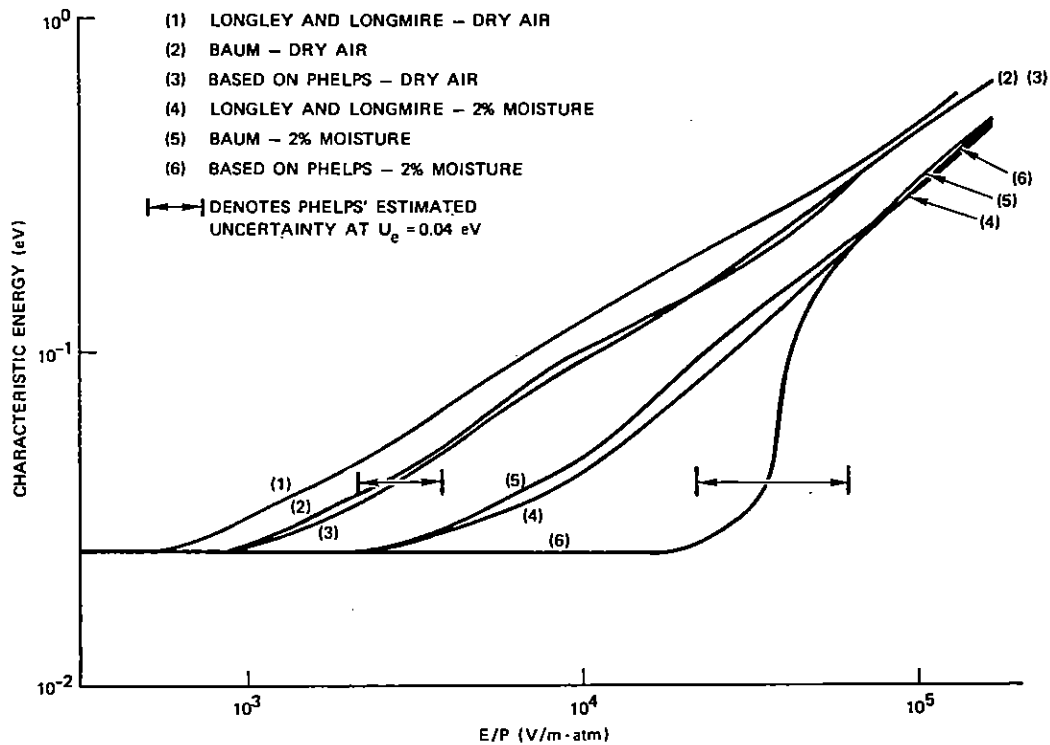


Figure 2. Electron Energy vs E/P

based on Phelps' compilation. In Figure 3 we have also plotted the various estimates for electron mobility as a function of E/P under the same conditions.

It may be seen that for dry air, Baum's model agrees closely with Phelps' estimates, while Longley and Longmire's model gives slightly higher electron energies and, at a given electron energy, slightly higher electron mobilities. For moist air, both EMP models predict substantially higher electron energies and, at a given energy, higher electron mobilities, as compared to the curves based on Phelps. The difference in predicted mobility for electrons in moist air is partly due to the approximate averaging process (described above) implicit

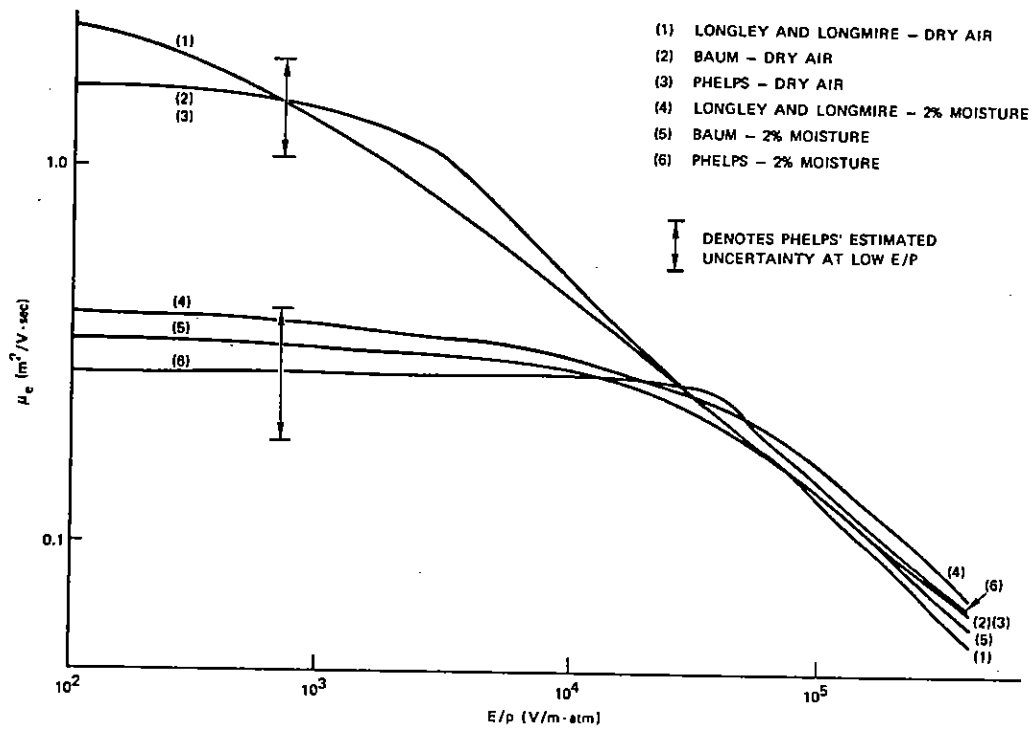


Figure 3. Electron Mobility vs E/P at 273°K

in the EMP models. Note the very abrupt rise in electron energy in the Phelps' curve for 2% moist air for E/P between 10^4 and 10^5 V/m·atm. This feature may not be fully consistent with the assumption of a Maxwellian electron energy distribution. Phelps' estimated uncertainty in this region is substantial: over +50% in E/P, perhaps a factor of three in electron energy.

It is also useful to compare the mobility predictions based on Phelps' compilation with some of the most recent experimental measurements. This is done in Figure 4. The measurement of electron mobility for thermal electrons in dry air, by Milloy et al. [5], which we have scaled to 273°K, agrees very well with the prediction based on Phelps' compilation.

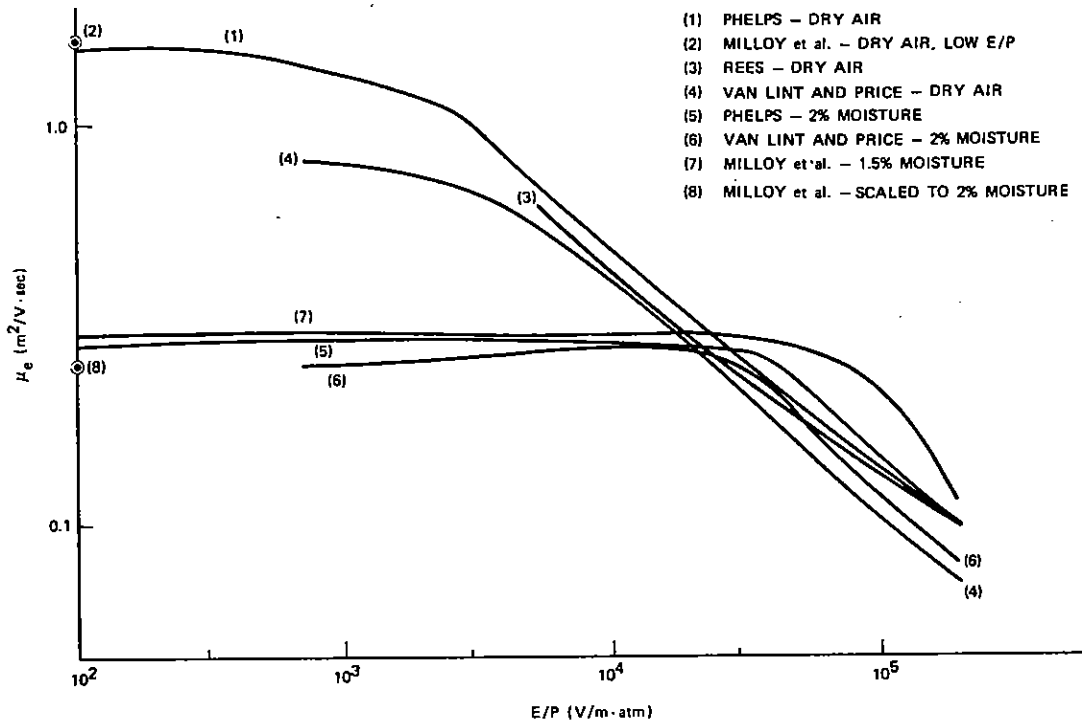


Figure 4. Comparison of Phelps' Compilation With Recent Data for Mobility vs E/P, Corrected to 273°K

The same is true for the measurements by Rees [6] of electron mobility in dry air as a function of E/P. (We have scaled Rees' curve, as reported by Milloy et al., to 273°K.) The dry air measurements by van Lint and Price [7] (also scaled to 273°K from 283°K) generally fall slightly below the other measurements, and the values based on Phelps. The discrepancy is substantial only at low E/P.

For moist air, the measurements at 1.5% water vapor content by Milloy et al. (scaled to 273°K) appear to be qualitatively consistent with the predictions based on Phelps (for 2% moisture) for $E/P \lesssim 10^5$ V/M·atm. The persistence in these data of nearly constant mobility out to $E/P \approx 10^5$ V/M·atm suggests that the electrons remain nearly thermal to even higher E/P

than implied by Phelps' compilation. We have also scaled the data of Milloy et al. according to the curve in Figure 1 to obtain the single "data" point for 2% moisture at very low E/P, again in reasonable agreement (~15%) with the values based on Phelps' compilation. The data of van Lint and Price for 2% moisture (scaled to 273°K from the experimental 293°K) also fall close to but slightly below the other values.

If we disregard the low E/P dry air data of van Lint and Price, it appears that electron mobility vs E/P calculations using the energy and momentum exchange rates compiled by Phelps are reasonably well substantiated by the more recent measurements, with, however, one major exception. This concerns the energy exchange frequency for electrons with water vapor. It is this quantity which has the greatest influence on the tendency of electrons in moist air to remain nearly thermal in energy for higher values of E/P than in dry air. Phelps attributes only order-of-magnitude accuracy to his estimates of this rate, for electrons above 0.04 eV. His more recent estimates of the energy exchange frequency are also 3 to 10 times larger than his earlier estimates (used by Baum). Furthermore, Crompton et al. [8] have recently described very preliminary measurements of D/μ for electrons in moist air which seem to imply energy exchange frequencies for electrons with water vapor even 3 to 10 times larger than Phelps' more recent estimates. Therefore, we conclude at present that there remains a very large uncertainty regarding the energy of electrons in moist air at E/P in the general range of 10^4 to 10^6 V/m·atm.

SECTION 2. ELECTRON ATTACHMENT

2.1 BACKGROUND

For characteristic energies less than about 1.0 eV, electron attachment in air is thought to be predominantly a three-body process in which a free electron combines with an oxygen molecule to form an unstable, vibrationally excited oxygen ion (denoted O_2^{-*}), which then either dissociates back to O_2 plus a free electron or else is stabilized by collision with a third body to yield an energetically stable O_2^- ion. Accordingly, one expects the attachment rate to be of the general form

$$\alpha = k_{O_2} N_{O_2}^2 + k_{N_2} N_{O_2} N_{N_2} + k_{H_2O} N_{O_2} N_{H_2O}$$

where N_{O_2} , N_{N_2} and N_{H_2O} are the species concentrations (molecules/cm³). The three-body rate coefficients are expected to depend only on the characteristic electron energy (or distribution function).

The more detailed theory of attachment, developed by Herzenberg [9], allows some insight into the dependence of the rate coefficients on the characteristic electron energy. In the first step of attachment, the formation of O_2^{-*} , the colliding electron-oxygen-molecule system must have the same total energy as one of the accessible ($v'=4,5,6,\dots$) vibrational states of O_2^{-*} . Effectively, this requires the electron involved to have a specific energy [10] $\epsilon \cong 0.09$ eV, 0.22 eV, 0.34 eV, When the formation and re-dissociation of O_2^{-*} in the various levels $v'=4,5,6, \dots$ occurs

more rapidly than the final stabilization process (i.e., the anticipated condition for sufficiently low pressures), one may express the steady-state, unstable, excited ion concentrations, $N(v')$, as

$$N(v') = k_{v'} \tau_{v'} N_{O_2} N_e f(\epsilon_{v'}) \Delta_{v'}$$

where $k_{v'}$ is the two-body rate coefficient with mono-energetic electrons of energy $\epsilon_{v'}$ (≈ 0.09 eV, 0.22 eV, . . .); $\tau_{v'}$ is the $O_2^{-*}(v')$ lifetime; N_e is the electron concentration; $f(\epsilon_{v'})$ is the electron energy distribution function evaluated at the relevant energy; and $\Delta_{v'}$ is the allowable energy interval (about $\epsilon_{v'}$). The overall three-body attachment coefficient with species X as a stabilizing third body may then be expressed as

$$k_x = K_x \sum_{v'=4}^{\infty} k_{v'} \tau_{v'} \Delta_{v'} f(\epsilon_{v'}) \xi_{xv'}$$

where K_x is the two-body rate coefficient for collisions between species X and O_2^- and where $\xi_{xv'}$ is the fraction of collisions between X and $O_2^{-*}(v')$ which lead to stabilization.

Detailed comparison of theory and data [10] for attachment of electron beams in low-pressure pure oxygen have indicated that $\Delta_4 k_4 \tau_4 \approx 1.7 \Delta_5 k_5 \tau_5 \approx 2.2 \Delta_6 k_6 \tau_6$, with the product $\Delta_{v'} k_{v'} \tau_{v'}$ decreasing more slowly for higher v' . Thus, for a Maxwellian distribution of electron energies, when $kT_e < 0.1$ eV, over 75% of the O_2^{-*} ions must be created in the lowest accessible ($v'=4$) level. Under these conditions, provided also that there are no special resonances causing

$\xi_{xv'}$, to be much larger for some higher level ($v' > 4$) than for $v'=4$, one expects

$$k_x \approx K_x \Delta_4 k_4 \tau_4 f(0.09 \text{ eV}) \xi_{x4} \quad (3)$$

Thus, the dependence of the rate coefficient on the characteristic electron energy (kT_e) is indicated to be approximately the same for all third bodies for $kT_e \lesssim 0.1$ eV, and determined by the electron temperature dependence of the distribution function evaluated at the first resonance (0.09 eV). This is a potentially very useful observation, for it suggests that one need measure the rate coefficient for any given third body at only one value of $kT_e \lesssim 0.1$ eV in order to have approximately determined the value for all $kT_e \lesssim 0.1$ eV.

If the stabilization efficiencies $\xi_{xv'}$, for $v' > 4$ are much smaller than ξ_{x4} , then the functional form just described will continue to apply for $kT_e > 0.1$ eV. This might possibly be the case with rare gas (i.e., single atom) third bodies. It may also be the case with the nitrogen molecule as a third body. In the opposite extreme, certain third bodies may have a very high stabilization efficiency ($\xi_{xv'} \approx 1.0$) for all of the lower-lying energetically accessible levels of O_2^{-*} (e.g., $v'=4,5,6$). Comparisons of theory and data [10] suggest that this is probably the case with the oxygen molecule as a third body. This may also be true with certain polyatomic molecules (e.g., C_2H_4 , C_2H_6 , H_2O) as third bodies. The above theory implies that the functional dependence of the rate coefficient k_x on the characteristic electron energy kT_e would again be identical for all such third bodies, although deviating from the simpler form of Equation 3 when $kT_e \gtrsim 0.1$ eV.

2.2 DATA FOR DRY GASES

It is interesting to test these conjectures by comparison with experimental data. This is partly done in Figure 5, which shows the measured dependence of the three-body attachment coefficients, for several different third bodies, on the characteristic electron energy kT_e . With each of the measured curves (solid lines) there is also plotted a theoretical curve (dashed line) based on Equation 3 assuming a Maxwellian electron energy distribution, normalized to the peak of the measured curve.

The measured curve shown for k_{O_2} is based on the data of Chanin et al. [11], but has been slightly decreased at low energies to agree with the data of Pack and Phelps [12] at thermal energy. This also agrees fairly well with the data point for k_{O_2} with thermal electrons ($k_{O_2} \approx 2.4 \times 10^{-30} \text{ cm}^6/\text{sec}$), reported by Shimamori and Hatano [13], and also with a number of other independent measurements [14].

The measured curve for k_{N_2} is also based on the data of Chanin et al., from oxygen-nitrogen mixtures. These data do not go below an indicated value of $kT_e \approx 0.06 \text{ eV}$. However, we have shown another data point for k_{N_2} for thermal electrons, from the measurements by Shimamori and Hatano, and a data point for $kT_e \approx 0.044 \text{ eV}$, from measurements by Pack and Phelps of k_{N_2} in oxygen-nitrogen mixtures at 477°K . The measured curves for $k_{C_2H_4}$ and $k_{C_2H_6}$ (which are essentially identical) are from the data of Goans and Christophorou [15].

It may be seen that, with the exception of k_{He} , the simple theoretical curve shape is in good agreement with the measured values. The slight deviation for k_{O_2} at $kT_e \gtrsim 0.1 \text{ eV}$ has been

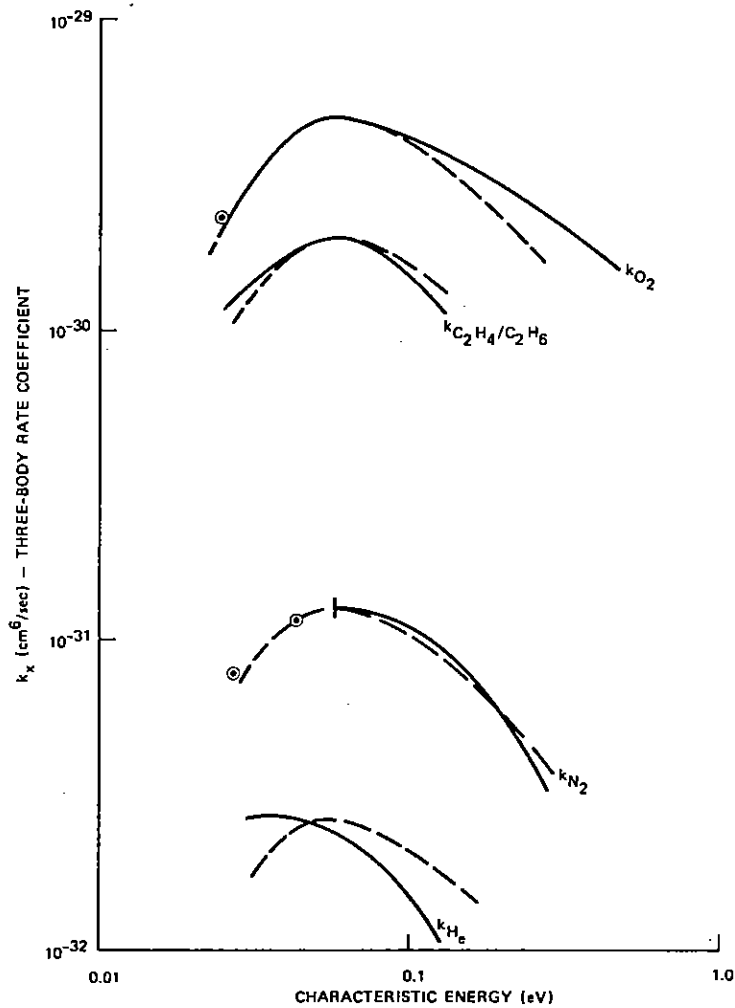


Figure 5. Partial Comparison of Data and Theory (Broken Curves) for Energy Dependence of Three-Body Attachment

attributed [10] to the contribution from the higher ($v'=5,6, \dots$) vibrational levels of the intermediate O_2^{-*} ion. Accepting this explanation, one sees that the maximum possible deviation from the simple theoretical curve could be as large as a factor of two, but only at the higher energies ($kT_e \sim 1.0$ eV).

Unfortunately, the situation in sea level air may be more complex than thus far indicated. All the data shown in Figure 5 were taken on gaseous mixtures with low (or zero) nitrogen pressure, $p_{N_2} \lesssim 200$ torr. Higher pressure data taken by McCorkle et al. [16] appear to reveal a basic change in the attachment process for $p_{N_2} \gtrsim 300$ torr. In Figure 6 we show the measured curve for k_{N_2} at $p_{N_2} \sim 1$ atm and for k_{O_2} at $p_{N_2} = 300$ torr, as compared with the theoretical curves and low (or zero) p_{N_2} measurements from Figure 5.

The differences between the k_{N_2} curves of McCorkle et al. and of Chanin et al. for $kT_e > 0.05$ eV have been attributed [16] to the use of an incorrect energy scale by Chanin et al., due to the non-Maxwellian form of the electron energy distribution. It may be seen that this difference may be as large as a factor of two in the attachment coefficient. At low electron energies, however, the difference between the k_{N_2} curve of McCorkle et al. and the low-pressure data (or the theoretical curve) is thought to be due to a change in the basic attachment mechanism [16]. The situation is made even more complicated by the fact that the low p_{N_2} data of McCorkle et al. (for k_{N_2} at $p_{N_2} = 300$ torr) are shifted downward from those in Figure 5 by nearly a factor of two, while still exhibiting the same functional dependence on kT_e . These anomalies are not adequately understood at present. The curve of McCorkle et al. for k_{O_2} shows a similar (but smaller) deviation from the low-pressure values.

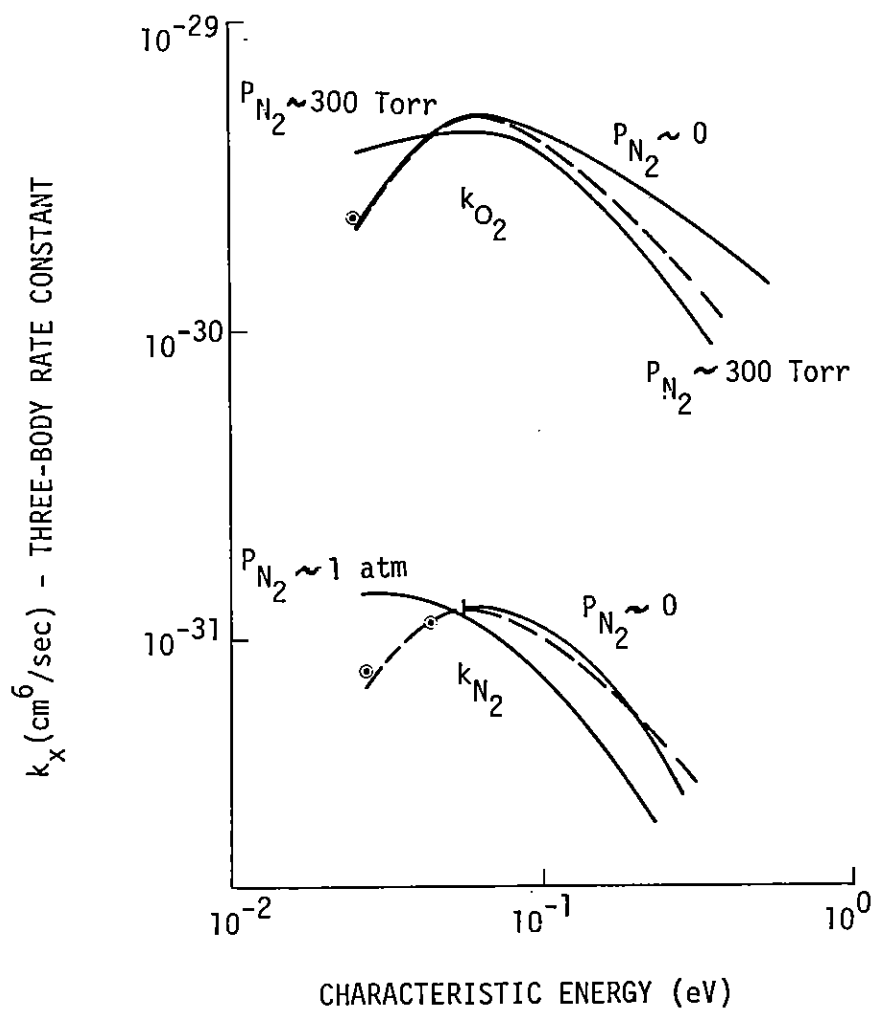


Figure 6. Comparison of Theory (Broken Curves) With Data For k_{N_2} and k_{O_2} at Low and High N_2 Pressure

By treating the P_{N_2} dependence of the k_{N_2} curve as a four-body process, Goans and Christophorou [15] obtained an effective four-body rate coefficient k_{N_2, N_2} with $(k_{N_2, N_2}) \div (k_{N_2}) \sim 8 \times 10^{-21} \text{ cm}^3$ (at $kT \sim 0.033 \text{ eV}$). This ratio is not too dissimilar from the ratio $(k_{O_2, O_2}) \div (k_{O_2}) \sim 4 \times 10^{-20} \text{ cm}^3$, reported by Shimamori and Hatanō [13] from low-pressure data (in fact, an analysis of Goans and Christophorou's data at $kT_e \approx 0.025 \text{ eV}$ gives somewhat better agreement), but a more definitive corroboration of these anomalous high nitrogen pressure effects is obviously needed.

Until recently, the only other potentially relevant data, of which we are aware, have been the measurements of attachment in dry air by Kapinos et al. [17], at total pressures up to 600 torr. These data imply an attachment rate for thermal electrons in dry sea level air of $8^{(+5)}_{(-2)} \times 10^7 \text{ sec}^{-1}$. By comparison, the rate which we would calculate at $N_{O_2} = 5 \times 10^{18} / \text{cm}^3$, $N_{N_2} = 2 \times 10^{19} \text{ cm}^3$, $k_{O_2} = 2 \times 10^{-30} \text{ cm}^6 / \text{sec}$, $k_{N_2} = 8 \times 10^{-32} \text{ cm}^3 / \text{sec}$, $(k_{N_2, N_2} / k_{N_2}) = (k_{O_2, N_2} / k_{O_2}) \approx (0.8 \text{ to } 4.0) \times 10^{-20} \text{ cm}^3$ would be $(7 \text{ to } 12) \times 10^7 \text{ sec}^{-1}$, and without the four-body contribution the rate would be $6 \times 10^7 \text{ sec}^{-1}$. Again, firm conclusions cannot be drawn.

Quite recently, an additional set of data has become available from the measurements by van Lint and Price [7] of electron attachment in dry and moist air, mostly at $P = 0.25$ and 0.5 atm . We have plotted these newer data for dry air in Figure 7 (as the solid lines) separately for $P = 0.25 \text{ atm}$ and $P = 0.5 \text{ atm}$. For comparison, we have also plotted in Figure 7 the predicted attachment rates based on either the very low P_{N_2} data of Figure 5 (dashed line) or on the $P_{N_2} \approx 300 \text{ torr}$ form of the k_{O_2} curve (with $k_{N_2} = k_{O_2} / 40$) of Figure 6

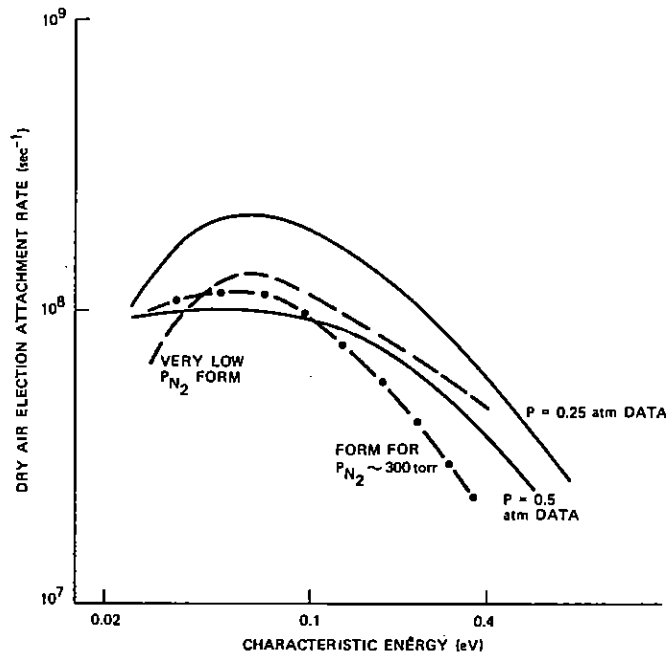


Figure 7. Comparison of Measurements of van Lint and Price with Predicted Attachment Rates (All Curves are Scaled to 1 atm and 2930K)

(dotted line). The E/P scale of van Lint and Price has been converted to kT_e using Phelps' curve in Figure 2.

It may be seen that the $P = 0.5$ atm data of van Lint and Price are qualitatively more similar to the predicted attachment curve based on the $P_{N_2} \sim 300$ torr data for k_{O_2} in Figure 6 than to the predictions based on the very low P_{N_2} data of Figure 5, while for the $P = 0.25$ atm data of van Lint and Price the opposite is true. This comparison could perhaps be further improved by use of a corrected energy scale for electrons in air. Thus, the data appear to qualitatively support the concept of an anomalous high-pressure effect on electron attachment to oxygen. A few additional data points (not shown) taken at $P = 1$ atm are also consistent with this trend. The probable reliability of this conclusion, and of the data, is lessened somewhat by a quantitative discrepancy of the

measurements for $P = 0.25$ atm. These lower pressure results, although exhibiting a functional form very similar to that predicted from the low P_{N_2} data of Figure 5 also appear to give attachment rates which are about 50% high in the absolute value, as compared to low P_{N_2} data from other sources.

2.3 ATTACHMENT IN MOIST AIR

Thus far, we have not discussed any data for k_{H_2O} , the three-body rate coefficient for electron attachment to oxygen with water vapor as a third body. The value of k_{H_2O} for thermal electrons ($T_e \approx 300-400^\circ K$) has been measured by Pack and Phelps [18], by Stockdale et al. [19] and by Bouby et al. [20], all of whom report a value $k_{H_2O} \approx 1.4 \times 10^{-29}$ cm⁶/sec, or about 6 to 7 times as large as the corresponding value of k_{O_2} . It may be seen from Figure 2 that electron energies in typical EMP fields ($E/P \lesssim 10^5$ V/m·atm) may exceed several tenths of an electron volt, even for fairly moist air. Thus, it is of interest to know the appropriate values of k_{H_2O} for the full range 0.025 eV $\lesssim kT_e \lesssim 0.7$ eV, and in a sea level air environment (e.g., $P_{N_2} \sim 600$ torr, $P_{O_2} \sim 150$ torr).

Based on the preceding theoretical discussion, it would appear reasonable to assume that k_{H_2O} varies with electron energy in the same manner as k_{O_2} , k_{N_2} , and the other rate coefficients. However, the exact form of this variation is uncertain, because of uncertainties regarding the correct energy scales and regarding the effects of background gas pressures. Moreover, the application of this simple theory to H_2O stabilized attachment may be questioned, since Equation 3, which implies that $k_{H_2O}/k_{O_2} \approx K_{H_2O}/K_{O_2}$, gives a predicted upper limit for

k_{H_2O} of 3 times k_{O_2} (about half the observed value), using $K_{O_2} \approx 10^{-9}$ cm³/sec [9] and assuming K_{H_2O} is not greater than the $H_2 + N_2H^+$ collision rate, 2.8×10^{-9} cm³/sec [21], since the ion-dipole interaction and the masses are essentially the same. A possible explanation may be that the stabilization efficiencies $\xi_{O_2, v'}$ ($v' = 4, 5, 6, \dots$), although essentially constant, are closer to one-half than to one, while $\xi_{H_2O, 4} \approx 1.0$.

With these various problems in mind, we show in Figure 8 two possible functional forms for k_{H_2O} for $0.025 \text{ eV} \lesssim kT_e \lesssim 0.7 \text{ eV}$.

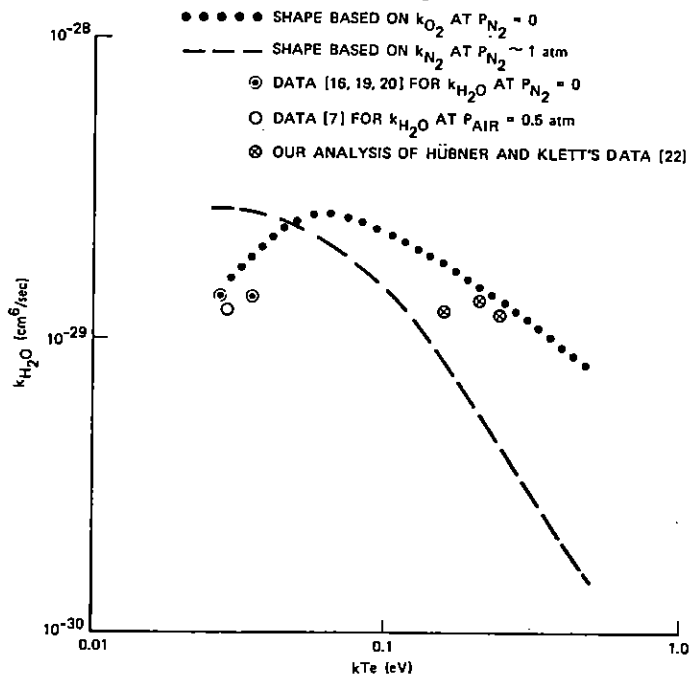


Figure 8. Possible Functional Forms for k_{H_2O} for Sea Level Air, Compared with Data

The dashed curve is based on the data for k_{N_2} at $P_{N_2} \sim 1$ atm. Thus, this curve reflects a possible anomalous non-three-body effect at high nitrogen pressures, and also a possible effect of non-Maxwellian electron energy distributions. The dotted curve is based on the data for k_{O_2} at zero P_{N_2} . Thus, this curve is essentially identical to Herzenberg's theory, including the possible effect of intermediate O_2^{-*} ions in higher vibrational states ($v' \geq 5$). The latter curve is normalized to pass through the measured [18-20] value $k_{H_2O} \approx 1.4 \times 10^{-29}$ cm⁶/sec for thermal electrons. The former curve is somewhat arbitrarily normalized to have the same peak value as the latter (compare Figure 6).

It is useful to compare these possible forms for k_{H_2O} with actual measurements for nonthermal electrons. Until quite recently, the only available data, as far as we are aware, have been those of Hübner and Klett [22] taken at $E/P = 5 \times 10^4$ V/m·atm in nitrogen at 760 torr total pressure with up to 2.5% oxygen and up to 2.3% water vapor. Using Phelps' compilation of energy and momentum exchange rates, we estimate $kT_e \approx 0.40$ eV for the dry N_2 and $kT_e \approx 0.16$ eV to 0.24 eV for the 1.4% to 2.3% water vapor mixtures. It must be kept in mind that these estimated electron energies in moist nitrogen are very uncertain and may be too high [8]. To estimate electron drift velocities needed for converting Hübner and Klett's basic data into attachment frequencies, we use the moist nitrogen data of Hurst et al. [23], which are also reasonably consistent with predictions based on Phelps' tabulations.

From the dry $N_2:O_2$ data of Hübner and Klett, we find $k_{N_2} \approx (0.5 \text{ to } 1.5) \times 10^{-32}$ cm⁶/sec, and $k_{O_2} \approx (0.9 \text{ to } 1.4) \times 10^{-30}$ cm⁶/sec. It may be seen that the k_{O_2} value is in better agreement with the empirical high-nitrogen-pressure

curve in Figure 6 than with the low or zero N_2 pressure curve of Chanin et al. As for the mixtures with 1.4% to 2.3% water vapor, using the empirical high P_{N_2} curves to subtract the effects of nitrogen and oxygen as third bodies, we obtain values of $k_{H_2O} \approx (1.2 \text{ to } 1.4) \times 10^{-29} \text{ cm}^6/\text{sec}$ at $kT_e \approx 0.16$ to 0.24 eV . These data points are also plotted in Figure 8 as \otimes .

From their very recent measurements of electron attachment in moist air at low E/P , van Lint and Price [7] infer a value of $k_{H_2O} \approx 1.2 \times 10^{-29} \text{ cm}^6/\text{sec}$ for thermal electrons. This value does not conflict too strongly with the other measurements cited above (which were at zero nitrogen pressure). We have also examined the basic data in their published form, and have concluded that they probably are not inconsistent with any value of k_{H_2O} in the general range of about $(1.0 \text{ to } 1.8) \times 10^{-29} \text{ cm}^6/\text{sec}$. We have plotted van Lint and Price's data point in Figure 8 as the open circle. Although van Lint and Price have also published measurements of attachment (for nonthermal electrons in moist air, they have not attempted to infer values of k_{H_2O} for nonthermal electrons from these data. We have made only a very tentative effort to extract values of k_{H_2O} at elevated electron energies from van Lint and Price's measurements of attachment in air with 2% water vapor, and have found that the uncertainties in electron energy, in the effectiveness of oxygen as a third body at elevated energies and nitrogen pressures, and in the data themselves make a consistent determination of k_{H_2O} vs kT_e very difficult. A more complete analysis of these measurements would probably provide better results, although the uncertainties in the data, in k_{O_2} , in the mean electron energy and possibly also in the energy distribution function would still limit the accuracy achievable.

2.4 ADDITIONAL PROBLEMS

The preceding discussion has assumed that the autodetachment rate (τ_v^{-1} , in Equation 3) for O_2^{-*} in a given level is much faster than the rate of collisional stabilization (e.g., $N_x K_x \xi_{xv}$, for a single third body). However, this may not always be the case; and we are thus provided with a further potential source of concern regarding electron attachment rates in (especially) moist, sea level air. As pointed out in Reference 14, the value of τ_4 is very uncertain, particularly at higher nitrogen pressures. However, theoretical calculations imply that τ_4^{-1} may be of the order of 10^{10} sec^{-1} . This value should be compared with the quantity

$$R \equiv K_{H_2O} \xi_{H_2O,4} N_{H_2O} + K_{O_2} \xi_{O_2,4} N_{O_2} + K_{N_2} \xi_{N_2,4} N_{N_2}$$

for sea level moist air. Using the "nominal" values $K_{O_2} \xi_{O_2,4} \approx 10^{-9} \text{ cm}^3/\text{sec}$, with $K_{H_2O} \xi_{H_2O,4} \approx 6K_{O_2} \xi_{O_2,4}$ and $K_{N_2} \xi_{N_2,4} \approx 1/40 K_{O_2} \xi_{O_2,4}$, we would obtain a collisional stabilization rate for sea level air (at 273°K) with 0% to 2% moisture of $(5 \text{ to } 9) \times 10^9 \text{ sec}^{-1}$, quite close to the "nominal" value of τ_4^{-1} . If collisional stabilization of O_2^{-*} should really be this rapid compared to autodetachment, then the net rate of attachment would be limited by the rate of formation of O_2^{-*} , so that it would no longer increase like P^2 at high pressure.

Such a saturation effect has not thus far been reported, even though measurements have been made (separately) in oxygen at up to 150 torr [24], dry air up to 600 torr [17], nitrogen up to 10,000 torr [16], and 2.3% water vapor (in sea level nitrogen [22]). Thus, either one or more of the above assumptions must be in error or else the various measurements have not

been sufficiently precise to reveal the anticipated effect, particularly if in competition with possible non-three-body effects at high nitrogen pressures.

The possibility of incomplete electron energy equilibration is another potential source of uncertainty in EMP air chemistry. Most electrons are created with energies of greater than 5 eV. If they are attached before coming into energy equilibrium with the gas and the electric field, then their mobility and attachment rate will differ from the equilibrium values. This effect was mentioned by van Lint and Price as a possible explanation of the differences between their 0.25 atm and 0.5 atm dry air data.

Baum has estimated the rate of energy equilibration for electrons in sea-level air [3] and has concluded that equilibration is typically much faster than attachment, so that equilibrium electron energies may be assumed. However, Baum's fits to the energy and momentum exchange rates do not do full justice to the data at $kT_e \lesssim 0.1$ eV. Therefore, we have performed a few additional calculations. We find that nonequilibrium may increase the effective attachment rate at $E/P \lesssim 3$ kV/m in 0.5 atm air by up to perhaps 30% at moderately early times, due to electrons attaching as they pass through the energy region of maximum cross section. This is in the wrong direction to explain the differences between the 0.25 and 0.5 atm data. The effect of nonequilibrium may also be present in some EMP situations, though only at low E/P in dry air near sea level.

2.5 ATTACHMENT RATES AS A FUNCTION OF E/P

In practical EMP problems the electron attachment rate is usually needed for specified values of E/P and air moisture

content. Given the latter parameters, the attachment rate can be calculated by first determining the mean electron energy for the conditions of interest. The mean electron energy is then used to determine the attachment rate coefficient from Figures 6 and 8. However, when direct measurements of attachment versus E/P in mixtures of practical interest are available, it is not necessary to assign mean electron energies or to determine the energy dependence of the basic rate coefficients k_{O_2} , k_{N_2} and k_{H_2O} .

Figure 9 and 10 show the attachment rates measured very recently by van Lint and Price [7] for dry air and air with 2% moisture, respectively, converted by them to 1 atm and 293°K. Also shown are curves calculated using the prescription of Longley and Longmire [4], which involves computing the mean electron energy, as shown in curves (1) and (4) of Figure 2, using the conventional low-pressure values of k_{O_2} (see Figure 5), and assuming $k_{N_2} = k_{O_2}/50$ and $k_{H_2O} = 8 k_{O_2}$. The resulting curves have a somewhat different shape from the measurements of van Lint and Price, but generally lie within ±40% of them.

Also included on these figures are curves based on the more recent energy-transfer values of Phelps [2] (see curves (3) and (6) of Figure 2), on the attachment data of McCorkle et al. [16] at high N_2 pressures (see Figure 6), and the relation $k_{H_2O} = 7 k_{O_2}$ from the thermal electron data [18-20]. The resulting attachment rates below about 10^4 V/m·atm are nearly constant, like the measurements of van Lint and Price, but are 30% to 50% larger, while at higher E/P values they cross over and become lower. Overall, the agreement is not significantly better than for the Longley and Longmire curves. A fourth set of curves is also included, based again on electron energies deduced from Phelps, but using the low N_2

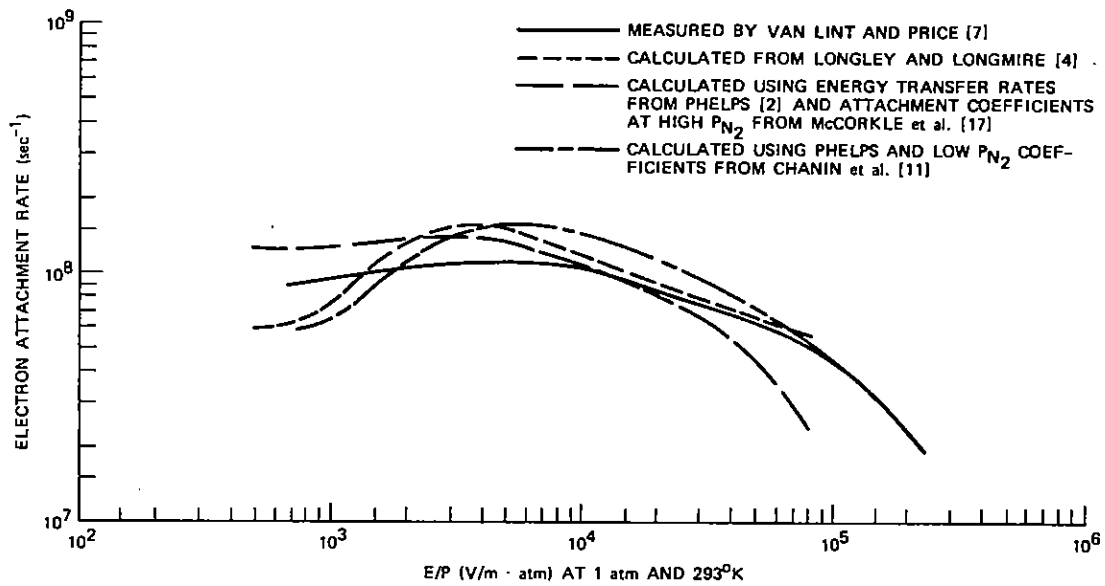


Figure 9. Measured and Calculated Electron Attachment Rates in Dry Air

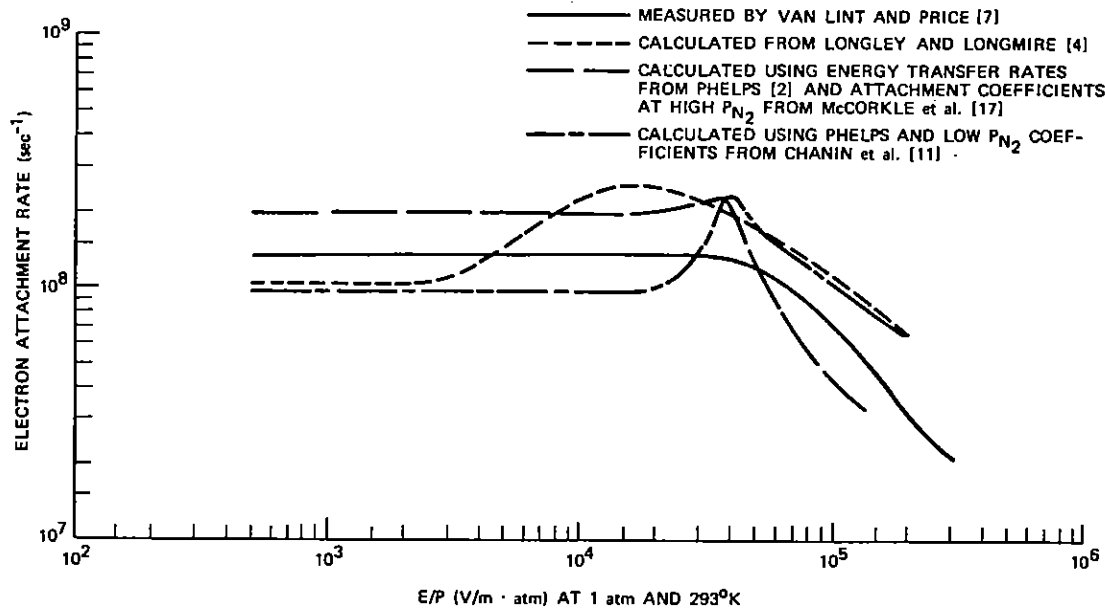


Figure 10. Measured and Calculated Electron Attachment Rates in Air With 2% Moisture

pressure data for attachment [11] and assuming $k_{\text{H}_2\text{O}} = 7 k_{\text{O}_2}$. These curves have somewhat different shapes from other curves, but their general deviation from the measurements is comparable. One could considerably improve the agreement of the calculations with the recent measurements by adjusting the individual attachment coefficients by not unreasonable amounts. However, in view of the uncertainties in the measurements, such an adjustment does not appear to be warranted at the present time.

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