ATTACHMENT-DETACHMENT IN AIR

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Resume:

The objective of this notebook is to review the available data and mechanisms for electron attachment and detachment and ion stabilization for dry air at E/n near the cross over between net attachment and ionization.

Referencing:

A.V. Phelps, private communication, http://www.lxcat.laplace.univ-tlse.fr.

Attachment-detachment in air

Setup notebook enviroment

```
In[8]:= now = StringForm["``/``/`` ``:``:``", Date[][[2]],
          Date[][[3]], Date[][[1]], Date[][[4]], Date[][[5]], Date[][[6]]]

Out[8]= 12/14/2010 19:36:30.2138097`9.232780396836816

In[9]:= SetDirectory["c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment"]

Out[9]= c:\users\avp\documents\mathbook\air\attachmentdetachment
```

The objective of this notebook is to review the available data and mechanisms for electron attachment and detachment and ion stabilization for dry air at E/n near the cross over between net attachment and ionization.

Graphs comparing the various results are at the end of this notebook. To open the various sections double click on the arrows at the right hand border. Many of the file manipulation commands are left in the old *Mathematica* format. One that does not appear to work is to "view file" using !!.
For several years I have not attempted to keep this up to date or to finish incomplete references and summaries.

Swarm experiments and models

- **Geballe and Harrison, Phys. Rev. 85, 372 (1952)**

- **Harrison and Geballe, Phys. Rev. 91, 1 (1953)**

- **Burch and Geballe, Phys. Rev. 106, 183 and 188 (1957)**

Conditions: 9 < E/p 50 V/cm Torr, 7 < pd < 26 Torr cm, 4 cm dia
Measured mobilities of three ions from rather indistinct structure in current following a photon induced electron pulse. Presents arguments for identifying them as O- at low and moderate E/p, O3- at low and moderate E/p, and O2- at moderate and high E/p.

- **Prasad and Graggs, Proc. Phys. Soc. (London) 77, 385 (1961)**

Note that Dall'Armi and Fletcher (2002) say that the data of Prasad and Graggs (1961) has been reanalyzed by Wagner (1971) to include detachment and yields lower ionization coeffieicnts.

- **Eiber, Z. Angew. Phys. 15, 103 (1962)**

Determined mobilities of three negative ions and one positive ion from time dependence of current and from frequency dependence of current in synchronous multiple shuttered drift tube. The scatter in the data was rather large. Negative ions are identified as O-, O3- and O2-. Discusses processes responsible for loss of O2- and production of O3-.

Dutton, Harris, and Llewellyn-Jones, Proc. Phys. Soc. (London) 81, 52 (1963)

Determine spatial ionization and attachment coefficients for electrons in air from spatial growth of ionization for 90 < E/n < 115 Td and 100 < p < 300 Torr. Do not consider detachment. While net ionization coefficients agree with previous values, the attachment coefficients are much smaller.

```
In[16]:= frommholdDetTable = Table[{#[[j, 3]], #[[j, 4]]}, {j, Length[#]}] &[
           Drop[Import["frommholddet.txt", "Table"], 5]];
```

Prasad and Graggs, Electronics Lett. ???? (1965)

A reexamination of measurements from Prasad and Graggs (1961) and Harrison and Geballe (1953) of current growth in uniform electric field in O2. Claim that for 34 < E/p <37 V/Torr cm detachment is barely detectable or absent for pressures above 100 Torr, but is measurable at lower pressures.

Feshenfeld et al, J. Chem. Phys. 45, 1844 (1966)

Associative detachment in flowing afterglow.

Moruzzi and Phelps, J. Chem. Phys. 45, 4617 (1966)

Mass spectrometer measurements of unnormalized fluxes of [O3-]/[O-] show the three-body behavior of the O- + 2 O2 -> O3- + O2 reaction at E/n = 16 Td and pressures of 1 - 3 Torr. The [O2-]/[O-] ratio is consistent with a two-body behavior of the O- + O2 -> O2- + O reaction at E/n = 83 Td at pressures of 0.9 to 2 Torr. At 90 Td the [O2-]/[O-] ratio is significantly larger and the pressure dependence is somewhat faster at pressures of 0.9 to 2 Torr.

Ryzko, H and Astrom E., J. Appl. Phys. 38, 328 (1967)

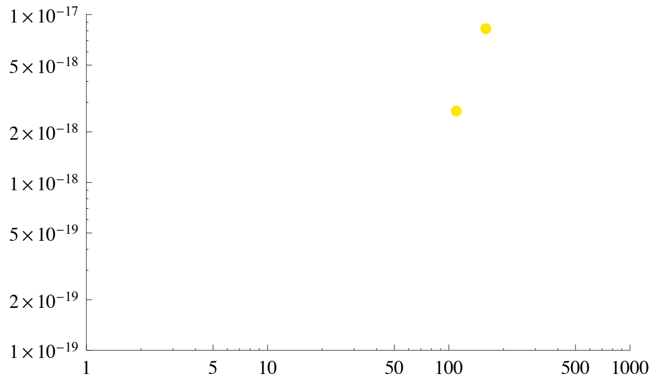
Discharge parameters: 100 < E/n < 160 Td, 4.4 < p20 < 60 Torr, 4.5 < d < 6 cm.
The experiments used the integrated current following a 40 ns uv pulse to produce photoelectrons. He did not consider negative ion stabilization. Note that the scatter in Ryzko's data is rather large, e.g., a factor of two.

Attachment coefficients

Says attachment coefficients are increase from 0.007 and 0.016 cm^-1Torr^-1 for 100 and 160 Td and are roughly equal to those of Frommhold (1964), but incease wth increasing E/p. The electron drift velocities wFit used to convert the spatial attachment coefficients to rate coefficients are from Phelps (1987).

```
In[18]:= wFit = 7.*10^3*eontd^0.45*(1+(eontd/13)^2)^0.18;

In[19]:= nuonAttRyzko = {0.007,0.0160}*100/(3.3*10^22)*(wFit /. eontd -> {110,160});  (*cm^-1TOrr^-1*

In[20]:= nuonAttRyzkoTable = Transpose[{{110,160},nuonAttRyzko}]

Out[20]= {{110, 2.66241 × 10^-18}, {160, 8.23258 × 10^-18}}
```

In[21]:=
```
ryzkoAttPlot = ListLogLogPlot[nuonAttRyzkoTable,  PlotRange -> {{1.,1000},{10^-19,1.01*10^-17
PlotStyle -> {Hue[0.15],PointSize[0.02]},  DisplayFunction->Identity]
```

Out[21]=


- **Detachment coefficients**

Derived negative ion lifetimes times pressure vary from 30 to 1.8 us torr for E/n of 100 and 160 Td. These values are somewhat smaller than those of Frommhold (1964).

In[22]:=
```
nuonDetRyzko = {1/30.,1/1.8}/10^-6/(3.3*10^22);   (*m^3/sec*)
```

In[23]:=
```
nuonDetRyzkoTable  = Transpose[{{110,160},nuonDetRyzko}]
```

Out[23]= $\{\{110,\ 1.0101\times10^{-18}\},\ \{160,\ 1.6835\times10^{-17}\}\}$

In[24]:=
```
ryzkoDetPlot = ListLogLogPlot[nuonDetRyzkoTable,  PlotRange -> {{0.1,1000},{10^-19,1.*10^-16}
PlotStyle -> {Hue[0.15],PointSize[0.02]}];
```

- **Hessenauer, H., Z. Phys. 204, 143 (1967)**

Drift tube measurements of attachment coefficients and drift velocities in air.

- **Sukhum, Prasad, and Graggs, Brit. J. Appl. Phys. 18, 785 (1967)**

Measurements of current growth in uniform electric field in O2. Say detachment is negligible for pressures above 50 Torr. They give detachment coefficients for lower pressures. The detachment coefficients vary from 4e-4 cm^-1 Torr^-1 at 35 V/cm Torr to 3e-3 cm^-1 Torr^-1 at 40 V/cm Torr, while the ionization and attachment coefficients are nearly constant at 0.1 cm^-1 Torr^-1.

- **Dutton and Howells, J. Phys. B 1, 1160 (1968)**

Determine mobilities for three negative ions and two positive ions using four-gause electrical shutter drift tube. Also, determined D/mu values for two positive ions. Identify positive ions as O2+ and O4+ and discuss equiliblrium amomg these ions.

- **Moruzzi, Ekin, and Phelps, J. Chem. Phys. 48, 3070 (1968)**

These are measurements of detachment in O2 - H2 mixtures. Although not mentioned in this paper, the data of Fig. 2 yields an upper limit to the rate coefficient for detachment in O2- + O2 collisions of 7.5e-10 * 2e-4 = 1.5e-13 cm^/s = 1.5e-19 m^3/s at E/p = 5 V/cm Torr = 15 Td. Pack and Phelps, J. Chem. Phys. 44, 1870, (1966) give values as low as 1e-16 cm^3/s = 1e-22 m^3/s at 0.1 Td and 375 K and 2.3e-21 m^3/s at E/n = 1 Td and 477 K.

- **Naidu and Prasad, J. Phys. B 3, 957 (1970)**

- **Kinsman and Rees, Int. J. Mass Spectrometry and Ion Phys. 5, 71 (1970)**

- **McKnight, Phys. Rev. A 2, 762 (1970)**

- **Eccles, O'Neill, and Craggs, J. Phys. B 3, 1724 (1970)**

Conditions: 135 < E/p < 150 V/cm Torr, 20 < pd < 60 Torr cm, 4 cm dia
A drift tube is divided into two sections by a grid. Section 1(E/p = 1 V/cm Tott and d1 = 3 cm) is used to produce oxygen negative ions. Section 2 (d2 = 0.5 to 1cm) is used to look for electron production by collisional detachment and subsequent ionization. Using other sources of ionization and attachment coefficient data they determine the detachment coefficient. The results are summarized by a detacment coefficient of ~ 0.01 cm^-1Torr^-1 at E/p ~ 140 V/cm Torr.

- **Snuggs et al, Phys. Rev. A 3, 487 (1971)**

- **Wagner, K. H., Z. Phys. 241, 258 (1971)**

Discharge parameters: 110 < E/n < 130 Td, 150 < p20 < 244 Torr, 4.5 < d < 6 cm. Gives relative mass spectrometer fluxes for O- and O2-.
Apparently the time-integrated total currents on the time scale of a few electron transit times were analyzed in terms of spatially independent ionization, attachment, detachment, and ion stabilization coefficients. Says longer drift distance gave better relative time resolution.

Claims that O- + 2 O2 -> O3- + O2 and O- + O2 + N2 -> O3- + N2 are not important at pressures used.

- **Ionization coefficients**

Says ionization coefficients differ insignificantly from those of Harrison and Geballe (1953) and Frommhold (1964).

- **Attachment coefficients**

Says attachment coefficients are close to 21% of the O2 values, actual values are constant at 0.017 cm^-1Torr^-1 for 110 < E/n < 130 Td. Points out that these values are about twice those of Frommhold (1964) and of Rysko (1967), where ion stabilization by charge transfer was neglected.
The electron drift velocities wFit used to convert the spatial attachment coefficients to rate coefficients are from Phelps (1987).

```
In[25]:= nuonAttWagner = 0.017*100/(3.3*10^22)*wFit /. eontd -> {110,130}  (*cm^-1TOrr^-1*)
```

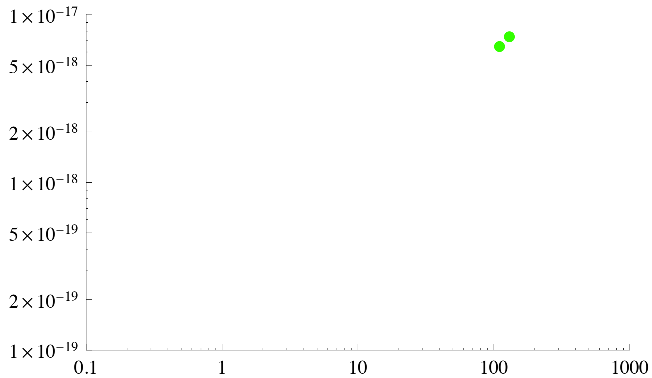
Out[25]= $\{6.46585 \times 10^{-18}, 7.39751 \times 10^{-18}\}$

```
In[26]:= nuonAttWagnerTable = Transpose[{{110,130},nuonAttWagner}]
```

Out[26]= $\{\{110, 6.46585 \times 10^{-18}\}, \{130, 7.39751 \times 10^{-18}\}\}$

In[27]:=
```
wagnerAttPlot = ListLogLogPlot[nuonAttWagnerTable, PlotRange -> {{0.1,1000},{10^-19,1.01*10^
PlotStyle -> {Hue[0.3],PointSize[0.02]}, DisplayFunction->Identity]
```

Out[27]=



- **Detachment coefficients**

Derived detachment coefficients are roughly a factor of two larger than for pure O2 , actual values are 0.25, 0.5, and 0.8 cm^-1-Torr^-1 for E/n of 110, 120, and 130 Td. He points out that these values are more than an order of magnitude larger than corresponding attachment coefficients.

Note that the detachment and charge transfer coefficients are defined in terms of the ion drift velocity, not the electron drift velocity. The detachment rate coefficients are evaluated under Davies (1983).

He assumes that the normalized negative ion mobility is 3.4 cm^2/V s at 760 Torr and 20 deg or .

In[28]:=
```
3.4*2.75*10^19*eontd*10^-17/100  /. eontd -> {110.,120.,130.}          (*m/s*)
```

Out[28]= {1028.5, 1122., 1215.5}

nuon is rate coefficient k

In[29]:=
```
nuonDetWagner = {0.25,0.5,0.8}*100/(3.22*10^22)*(3.4*2.75*10^19*eontd*10^-17/100  /. eontd ->
```

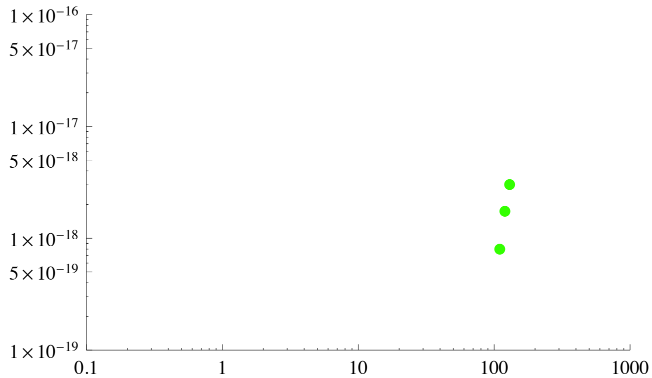
Out[29]= $\{7.98525\times10^{-19},\ 1.74224\times10^{-18},\ 3.01988\times10^{-18}\}$

In[30]:=
```
nuonDetWagnerTable = Transpose[{{110.,120.,130.},nuonDetWagner}]
```

Out[30]= $\{\{110.,\ 7.98525\times10^{-19}\},\ \{120.,\ 1.74224\times10^{-18}\},\ \{130.,\ 3.01988\times10^{-18}\}\}$

In[31]:=
```
wagnerDetPlot1 = ListLogLogPlot[nuonDetWagnerTable,  PlotRange -> {{0.1,1000},{10^-19,1.*10^-
PlotStyle -> {Hue[0.3],PointSize[0.02]}]
```

Out[31]=



- **Ion stabilization**

Derived negative ion stabilization coefficients that vary from 0.09, 0.12, and 0.15 cm^-1Torr^-1 for E/n of 110, 120, and 130 Td. He claims that these values are 21% of pure O2 values. although the graph shows ~ 16%.

- **Parkes, Trans. Faraday Soc. 67, 711 (1971)**

Mass spectrometer studies of negative ions from an O2 drift tube. Conditions: 0.1 < E/n < 60 Td, 0.5 < p < 10 Torr, 8 cm length, 4.8 cm dia.

Looks at the [O3-]/[O-] and [O4-]/[O2-] ratios at the anode. I found the pressure dependencies of the results of this paper very confusing and suspect that the model used is over simplified. See Parkes, Vacuum 24, 561 (1974) for possible interpretation of these results.

- **Price, Lucas, and Moruzzi, J. Phys. D 5, 98 (1972)**

Measurements of steady-state ionization growth are in O2-H2 mixtures are used to get spatialionization coefficients for pure O2 in the absence of attatchment, i.e., it is assumed that all O- formed by dissociative attachment quickly undergoes detachment in O- + H2 collisions. Their ionization coefficients for O2 are lower than most, but not all, previous values.

- **Frommhold, Goodson and Corbin, Phys. Lett. 45A, 51 (1973)**

Use measurements of the ratio of the charge collected in one electron transit time to the total charge collected to obtain the spatial inization coefficient for 14 < E/p < 160 V/cm Torr. A set of rate equations including attachmant, detachment, in conversion, and charge transfer were used to analyze the data. Details are not given.

Frommhold, Corbin, and Goodson, Phys. Rev. A 8, 1403 (1973)

Here they consider various analytic models of attachment, detachment and ion conversion. For me, this paper is best read after Goodson, Corbin, and Fromhold, Phys. Rev. A 9, 2049 (1974).

Skullerud, J. Phys. B 6, 728 (1973)

Lucas, Price, and Moruzzi, J. Phys. D 6, 1503 (1973)

Boltzmann calculation of electron transport and reaction coefficients for O2.

Price, Lucas, and Moruzzi, J. Phys. D 6, 1514 (1973)

Determine spatial ionization, apparent attachment coefficient from spatial growth of ionization in O2 for 90 < E/n < 150 Td and 10 < p < 100 Torr. Detachment coefficients are inferred from the difference between calculated and apparent attachment coefficients. Cite evidence that detachment also occurs from another negative ion.

O'Neill, and Graggs, J. Phys. D 6, 2625 (1973)

Using a drift tube and mass spectrometer at pressures of 20-60 Torr and E/n of 124 to 155 Td, they measured current growth and relative negative ion signals. A two section drift tube is used to vary the ion injected into the drift region that is sampled by the mass spectromenter. Claim negligible collisional dissociation of O3- to O-. Give tables of detachment and ion conversion coefficients.

Rebentrost, Chem. Phys. Lett. 21, 368 (1973) and Int. J. Mass Spectrom. and Ion Phys. 1, 475 (1973)

In the first paper he applies his model of ion-induced endothermic reactions - Chem. Phys. Lett. 17, 486 and 489 (1972) - to O- + O2 -> O2- + O and finds a threshold energy of 0.95 eV in center of mass.

In the second paper he applies his model of ion-induced endothermic reactions to O- + O2 -> e + O + O2 and O- + N2 -> e + N2 + O and find threshold energies of about 1.4 eV. He neglects associative detachment - O- + O2 -> e + O3 - on the basis of Feshenfeld et al (1966)

Goodson, Corbin, and Fromhold, Phys. Rev. A 9, 2049 (1974)

The discharge parameters are: 100 < E/n < 350 Td, 1 < p < 30 Torr, d = 2.54 cm. The principle result, shown in Fig. 3, is the frequency of electron detachment events in O2- + O2 collisions. Their argument is that the time scale of the decay of O- flux is so short that they essentially start with a cloud of O2- ions that collide with O2 to detach and to form stable O3-. They appear to assume that the O2- -> e -> O- -> O3- is so fast that they cannot detect the steps. The O4- ion is essentially neglected, as justified in part by mass spectrometer studies.

O- + O2 -> e + ? from Fig. 3

The digitized data from Fig. 3 is

In[32]:= `Import["goodson74.dat", "CSV"] // TableForm`

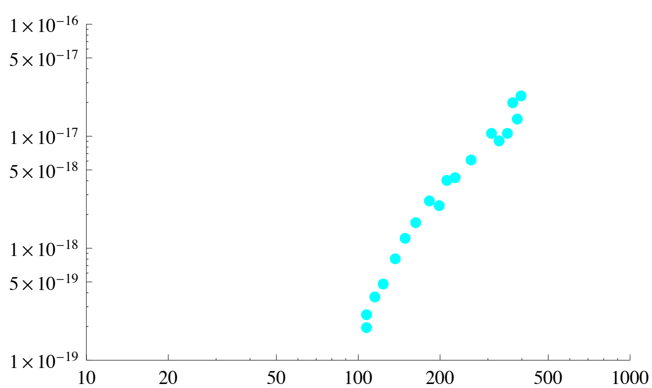
Out[32]//TableForm=

```
%Apparent detachment coefficient for O2- in O2
Fig. 3                                              Goodson    Corbin    and Fromhold    Ph
   %E/n (Td) kdet  (m^3/s)
   107.29    1.954e-19
   107.29    2.549e-19
   115.13    3.67e-19
   123.55    4.789e-19
   136.91    8.043e-19
   148.82    1.2246e-18
   162.8     1.69e-18
   182.7     2.646e-18
   198.6     2.399e-18
   211.8     4.029e-18
   227.3     4.261e-18
   260.1     6.135e-18
   309.3     1.0595e-17
   329.8     9.081e-18
   353.9     1.0595e-17
   370.2     1.99e-17
   384.7     1.422e-17
   397.2     2.29e-17
```

In[33]:= `goodson74DetTable = Drop[Import["goodson74.dat", "Table"], 3];`

In[34]:=
```
goodsonDetPlot =
 ListLogLogPlot[goodson74DetTable, PlotRange → {{10., 1000}, {10^-19, 10^-16}},
                     PlotStyle -> {Hue[0.5], PointSize[0.02]}]
```

Out[34]=



- **Formation of O2- and O3- by electron "attachment" from Figs. 5 and 6**

These authors describe the formation of O2- and O3- by effective "attachment" coefficients, i.e., the rate equation terms are proportional to the electron density rather than the O- density. This leads to strong pressure dependences of the coefficients because of competition between the two body processes of detachment and of charge transfer and the three body process of O3- formation. They attempt to include the effects of the competition between energy relaxation of the O- and its reactions with O2, i.e., the fact that the O- reactions can occur while the O- "remembers" its initial kinetic energy resuting from dissociative attachment. We note that his means that one should not use the Wanner or Rebentrost expressions for the O- energy distribution. See Parkes (1974) for other proposals.

Summary of this paper

In summary, the authors say that following the initial electron pulse, with its associated O- detachment and charge transfer reactions, there are delayed electrons resulting from detachment from O2- O2 collisions. They also say the data requires a stabilization process that fits O2- -> e -> O- -> O3-. They consider the fact that the O- energy distribution is not an equilibrium distribution. The estimated relative magnitudes of the detachment coefficients shown in their Fig. 4 is very useful for understanding the overall model.

Corbin and Frommhold, Phys. Rev. A 10, 2273 (1974)

In the third paper, electron growth measurements in O2-H2 mixtures yields an ionization coefficient for electrons in pure O2 of

```
In[35]:= 2.5*Exp[-170/eop] (*cm^-1Torr^-1 for V/cm Torr*);

In[36]:= alphaion = %/(3.3*10^22)  /. eop -> 0.33*eontd  (*m^2*)
```

Out[36]= $7.57576 \times 10^{-23}\, e^{-515.152/\text{eontd}}$

Parkes, Vacuum 24, 561 (1974)

This is a thorough review and analysis of experiments and models as of 1974 concerned with negative ion reactions in O2.

A major point of this paper is to question the use of a Maxwellian ion energy distribution with the temperature given by the Wannier relation. Parks advocates the Rebentrost model that gives a pronounced forward peak to the energy distribution caused by ions that travel several mean-free-paths without collision. The result of this is a reduction of the threshold energy for detachment in O- + O2 from 2.2 eV as found by Frommhold (1964) to 1.5 eV.

O- + 2 O2 -> O3- + O2

Parkes compares numerous sets of data in Fig. 10. We take a fit to the data to be

```
In[37]:= kIon3body = 1.*10^-30/(1+(eontd/65)^4)  (*cm^6/s*)
```

Out[37]= $\dfrac{1.\times 10^{-30}}{1+\frac{\text{eontd}^4}{17\,850\,625}}$

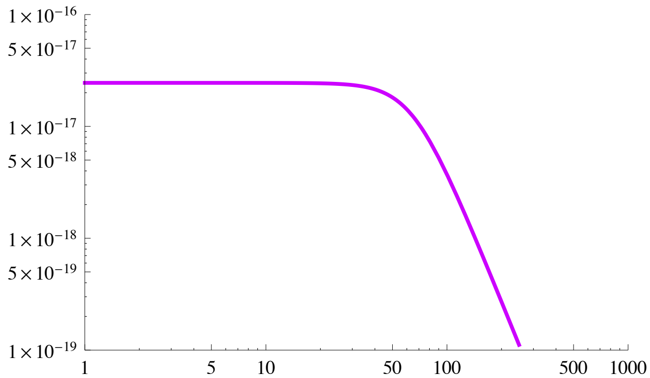
```
In[38]:= % /. eontd -> {1,10,80,100,150}
```

Out[38]= $\{1.\times 10^{-30},\ 9.9944\times 10^{-31},\ 3.03527\times 10^{-31},\ 1.51468\times 10^{-31},\ 3.40595\times 10^{-32}\}$

Parkes attributes this surprisingly fast decrease with increasing E/n to the inclusion of the back reaction, O3- + O2 -> O- + 2 O2, to give a net rate coefficient. We now make a plot of the effective 2-body reaction rate coefficient appropriate to atmospheric pressure so as to show the maximum effect of this process.

In[39]:=
```
parkes3bodyPlot = LogLogPlot[(kIon3body/10^12n /. n ->2.45*10^25), {eontd,1,250}, PlotRange
 PlotStyle -> {Hue[0.8],Thickness[0.007]}]
```

Out[39]=



Parkes estimates of the back reaction, i.e., the O3- dissociation rate coefficient, give values that are too small. He proposes other O3- destruction processes, i.e., O2- formation and detachment. This is an unsatisfactory situation.

- **O- + O2 -> O2- +O**

Parkes compares numerous sets of data in Fig. 11. We take a fit to the data to be

In[40]:=
```
kIon2body = 1.*10^-8*Exp[-900/eontd]/10^6   (*m^3/s*)
```

Out[40]= $1. \times 10^{-14}\, e^{-900/\mathrm{eontd}}$

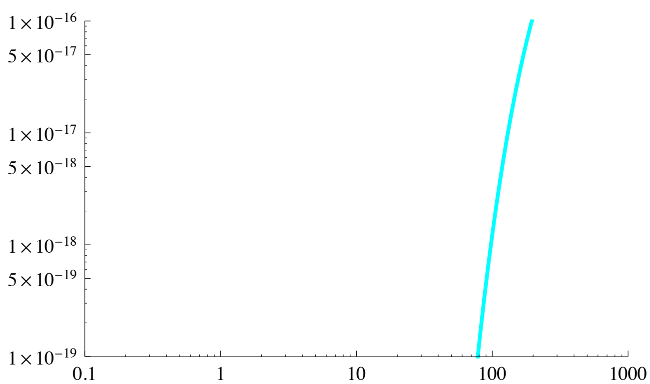
In[41]:=
```
% /. eontd -> {60,80,100,150,200}
```

Out[41]= $\{3.05902 \times 10^{-21}, 1.30073 \times 10^{-19}, 1.2341 \times 10^{-18}, 2.47875 \times 10^{-17}, 1.1109 \times 10^{-16}\}$

This looks like a reasonable fit at the E/n of Fig. 11, but extrapolates to unreasonably large values at higher E/N.

In[42]:=
```
parkes2bodyPlot = LogLogPlot[kIon2body, {eontd,10,250}, PlotRange ->{{0.1,1000},{10^-19,1.0*
PlotStyle -> {Hue[0.5],Thickness[0.007]}]
```

Out[42]=



- **O2- + O2**

Parkes points out that the endothermic reactions of O2-, such as dissociation to form O-, are inhibited by the large cross section of O2- with O2 which keeps the energy of the O2- small. He claims Frommhold's detachment rates for O2- + O2 are high.

O3-+O2

Parkes discusses the reactions leading to O-, O2-, and free electrons.

■ Lindinger et al, J. Chem. Phys. 63, 3238 (1975)

A flowing afterglow combined with a drift tube is used to show that the rate coefficient for O- + N2 -> e +? in an He buffer gas is less than 1e-12 cm^3/s for mean relative energies up to 2 eV. This is said to be much smaller than that calculated from the cross section reported by Comer and Schulz, Phys. Rev. A 10, 2100 (1974) ,i.e., 7e-12 cm^3/s for <enrel> of 0.5 to 1 eV.

■ Rayment and Moruzzi, Int. J. Mass Spectrometry and Ion Phys. 26, 321 (1978)

Discharge parameters: 3 < E/n < 120 Td, 0.25 < p < 2 Torr, d ~ 5 cm.
The experiments used a cross flow drift tube and measured the relative O- signal reaching the anode with a differentially pumped mass spectrometer. From the dependence of the O- signal on N2 pressure they obtain the loss of O- in collisions with N2.

The digitized data from Fig. 15 is

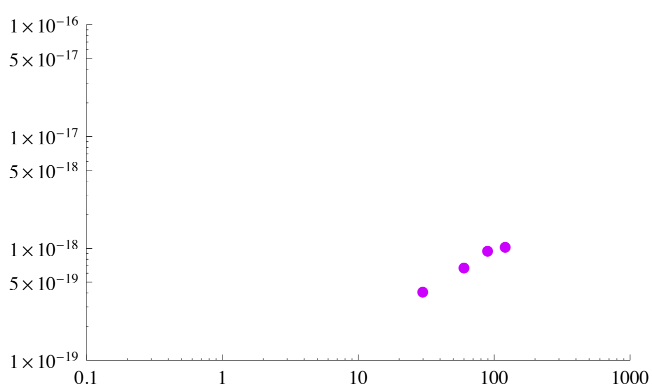
In[43]:=
```
Import["rayment78.dat", "CSV"] // TableForm
```

Out[43]//TableForm=
```
%Electron detachment rate coefficient by O- + N2 collisions
Fig. 4 of Rayment and Moruzzi                          Int. J. Mass Spectrom. and I
   %E/n  (Td) kdet (m^3/s)
   3.173      6.754e-21
   6.981      3.519e-20
   14.596     8.266e-20
   29.83      4.065e-19
   59.97      6.677e-19
   89.48      9.439e-19
   120.58     1.0233e-18
```

In[44]:=
```
rayment78DetTable = Drop[Import["rayment78.dat", "Table"], 3];
```

In[45]:=
```
raymentDetPlot =
 ListLogLogPlot[rayment78DetTable, PlotRange → {{0.1, 1000}, {10^-19, 10^-16}},
                     PlotStyle -> {Hue[0.8], PointSize[0.02]}]
```

Out[45]=



They interpret this data as the rate coefficient for the reaction O- + N2 -> e + N2O with a treshhold of ~ 0.2 eV.

Okada, Sakai, Tagashira, and Sakamoto, J. Phys. D 11, 1107 (1978)

A very graphic MC calculation showing the details of relaxation and charge transfer for O- in O2 following dissociative attachment. They calculate the drift velocities and diffusion coefficients for O- and O2- in O2. They present calculated detachment and charge transfer spatial coefficients for E/n from 80 to 200 Td. Unfortunately, they make no comparisons with coefficients calculated using the Wannier energy distributions. It would therfore be desirable to compare with other calculations.

Doussot, Bastien, Marode, and Moruzzi, J. Phys. D 16, 2451 (1982)

A variable-length, drift-tube with an attached mass spectrometer. Apparently, the objective was to determine the loss coefficients for O- by comparing the spatial and temporal dependences of the O- signal. It appears to me that this experimant was unsuccessful.

Davies, Theoretical Note No. 346, Westinghouse Research Laboratories, May 1983

An abstract covering this material appeared in Proc. XVIII Int. Conf. on Ionization Phenomena in Gases, Ed by Williams, Swansea 1987 p. 2. This report as DaviesNTIS-10-3-2010-1268251840303_fullDoc_ascii_.txt. The reports are also listed by NTIS as TN346 and TN352.

Discharge parameters: 0.6 < E/n < 225 Td, 30 < p0 = 100 Torr, 0.07 < d < 5.2 cm.
There are two modes of operation: 1) a 20 ns pulsed spark discharge was used to measure electron drift velocities and 2) a ~100 us pulsed discharge lamp was used to measure positive and negative ion currents to get ion mobilities and effective attachment coefficients for dry and moist air. One concern is the distortion of the electron pulse caused by delayed detachment and the resultant underestimate of the electron drift velocities. These experiments do not separate the effects of attachment, detachment, and ion conversion.

Effective attachment coefficient

In[46]:=
```
!! daviesatt.txt
```

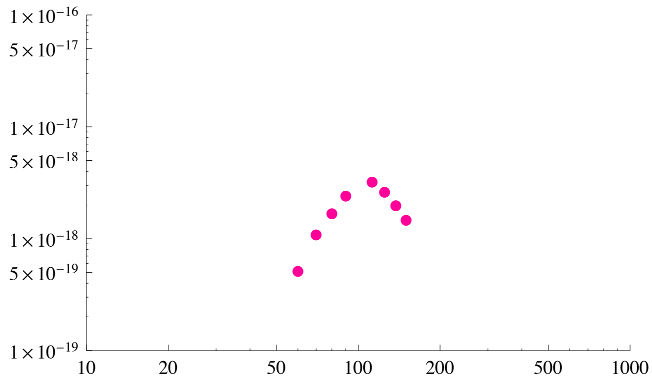
```
%Two-body attachment rate in dry air - D. K. Davies 1983

N            E/N      ENo/N    nuaNo/N     nua/N
1E22 m^-3  1E-21 Vm^2 1E4 V/m   1E7 s^-1   1E-18 m^3/s
%

265       60.0        161.3   1.37      0.51
133       70.0        188.2   2.9       1.08
133       80.0        215.0   4.5       1.67
133       90.0        241.9   6.4       2.4
66.6      112.5       302.4   8.5       3.2
30.6      125.0       336.0   7.0       2.6
25.8      137.5       369.6   5.3       1.97
19.4      150.0       403     3.9       1.46
```

Read in the data from this file and prepare plots.

In[47]:=
```
daviesAttTable = Table[{#[[j, 2]], #[[j, 5]] * 10^-18}, {j, Length[#]}] &[
    Drop[Drop[Import["daviesAtt.txt", "Table"], 6], -1]];
```

In[48]:=
```
daviesAttPlot =
 ListLogLogPlot[daviesAttTable, PlotRange → {{10., 1000}, {10^-19, 10^-16}},
          PlotStyle -> {Hue[0.9], PointSize[0.02]}]
```

Out[48]=



■ Electron drift velocity

In[49]:= **!! davieselectron.txt**

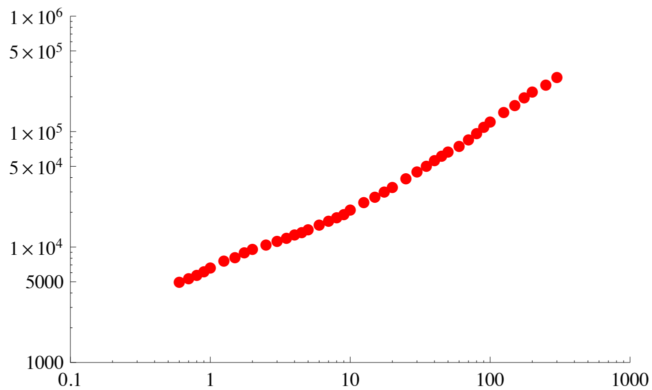
```
%From Davies and Chantry, Air Chemistry Measurements II, Theoretical Note 352, July 1984
TABLE 2.    VALUES OF THE   ELECTRON MOBILITY IN DRY AIR
E/N ENO/N   mueNmueN/No W
Td  10^4 V/m    10^24 /Vms  m^2/Vs  m/s
%
0.6 1.613   8.250.307   4950
0.7 1.882   7.590.282   5313
0.8 2.15    7.1 0.264   5680
0.9 2.419   6.780.252   6102
1   2.688   6.580.245   6580
1.25    3.36    6.040.225   7550
1.5 4.03    5.390.201   8085
1.75    4.7 5.090.189   8907.5
2   5.38    4.770.177   9540
2.5 6.72    4.160.155   10400
3   8.06    3.730.139   11190
3.5 9.41    3.4 0.127   11900
4   10.75   3.180.118   12720
4.5 12.1    2.960.1113320
5   13.44   2.820.105   14100
6   16.13   2.580.0961  15480
7   18.82   2.390.0887  16730
8   21.5    2.240.0832  17920
9   24.19   2.120.0789  19080
10  26.88   2.090.0777  20900
12.5    33.6    1.940.0723  24250
15  40.3    1.8 0.067   27000
17.5    47  1.710.0638  29925
20  53.8    1.640.061   32800
25  67.2    1.560.0582  39000
30  80.6    1.490.0556  44700
35  94.1    1.430.053   50050
40  107.5   1.4 0.0519  56000
45  121 1.36    0.0504  61200
50  134.4   1.330.0496  66500
60  161.3   1.240.0461  74400
70  188.2   1.210.0449  84700
80  215 1.2 0.0446  96000
90  241.9   1.210.0451  108900
100 268.8   1.210.045   121000
125 336 1.17    0.0434  146250
150 403 1.12    0.0417  168000
175 470 1.12    0.0417  196000
200 538 1.1 0.0407  220000
250 672 1.01    0.0375  252500
300 806 0.98    0.0366  294000
```

Read in the data from this file and prepare plots.

In[50]:=

```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\davieselectron.txt";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
data2 = Transpose[data1];
driftVelData= Transpose[{data2[[1]],data2[[5]]}];
daviesElectronVelPlot =  ListLogLogPlot[driftVelData,PlotRange -> {{0.1,1000.},{1000.,1000000.}},
                         PlotStyle -> {Hue[1],PointSize[0.02]}, DisplayFunction->Identity]
```

Out[58]=



■ Ion drift velocities

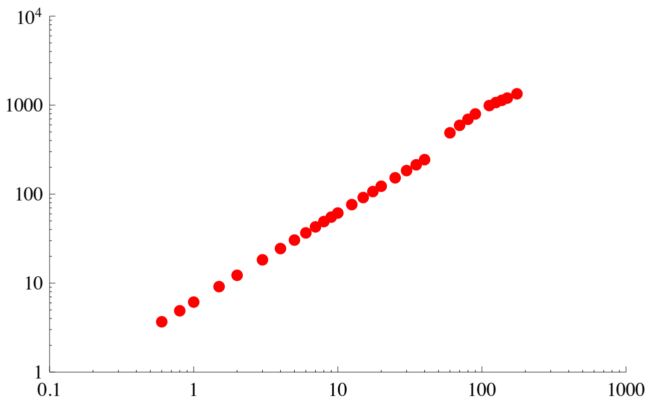
In[59]:= **!! daviesmobility.txt**

```
%From Davies and Chantry, Air Chemistry Measurements II, Theoretical Note 352, July 1984
TABLE 3. VALUES OF THE NEGATIVE-ION MOBILITY IN HUMID AIR (0.02 H20)
COMPARED WITH PREVIOUS MEASUREMENTS (REF. 1) IN DRY AIR
        ------f(H2O) = 0.0---------------------------           -----f(H2O) = 0.02---------
E/N ENo/N   mu-Nmu-No/N Wion    mu-N    mu-No/N
Td  10^4V/m 10^21/Vms   10^-4m^2/Vs m/s 10^2m^2/Vs  10^-4m^2/Vs
%
0.60    1.613   6.132.283.678   4.97    1.85
0.80    2.150   6.112.274.888   4.96    1.85
1.00    2.688   6.122.286.120   5.01    1.86
1.50    4.030   6.092.279.135   4.99    1.86
2.00    5.380   6.122.2812.24   4.97    1.85
3.00    8.060   6.092.2718.27   5.00    1.86
4.00    10.75   6.112.2724.44   4.96    1.85
5.00    13.44   6.092.2630.45   4.98    1.85
6.00    16.13   6.112.2736.66   4.97    1.85
7.00    18.82   6.122.3042.84   4.96    1.85
8.00    21.50   6.142.2849.12   4.98    1.85
9.00    24.19   6.132.2855.17   5.00    1.86
10.0    26.88   6.132.2861.30   4.99    1.86
12.5    33.60   6.102.2776.25   5.00    1.86
15.0    40.30   6.102.2791.50   5.61    1.86
17.5    47.00   6.102.27106.8   5.03    1.87
20.0    53.80   6.132.28122.6   5.00    1.86
25.0    67.20   6.102.27152.5   5.00    1.9
30.0    80.60   6.132.28183.9   5.03    1.9
35.0    94.10   6.102.27213.5   4.97    1.85
40.0    107.5   6.102.27244.0   5.00    1.86
60.0    161.3   8.143.03488.4   6.64    2.47
70.0    188.2   8.473.15592.9   6.91    2.57
80.0    215.0   8.663.22692.8   7.10    2.64
90.0    241.9   8.843.290   795.6   7.20    2.68
112.5   302.4   8.793.27988.8   7.39    2.75
125.0   336.0   8.553.181069.   7.47    2.78
137.5   369.6   8.233.061132.   7.50    2.79
150.0   403.0   8.002.981200.   7.53    2.80
175.0   470.0   7.662.851340.   7.50    2.79
```

Read in the data from this file and prepare plots.

In[60]:=
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\daviesmobility.txt";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
data2 = Transpose[data1];
ionVelocityData= Transpose[{data2[[1]],data2[[5]]}];
daviesIonVelocityPlot =  ListLogLogPlot[ionVelocityData,PlotRange -> {{0.1,1000},{1.,10000.}}, PlotStyle -> {
                          PointSize[0.02]}, DisplayFunction->Identity]
```

Out[68]=



In the following we limit the fitting to the last 9 points, i.e., the values that appear to give the O- mobility in dry air. The lower E/n points appear to apply to O2- in dry air.

In[69]:=
```
daviesIonVelocity  = Interpolation[Take[ionVelocityData,-9]];
```

- **Evaluation of Wagner's detachment frequencies**

Derived detachment coefficients are roughly a factor of two larger than for pure O2 , actual values are 0.25, 0.5, and 0.8 cm^-1-Torr^-1 for E/n of 110, 120, and 130 Td. He points out that these values are more than an order of magnitude larger than corresponding attachment coefficients.

In[70]:=
```
nuonDetWagner2  = {0.25,0.5,0.8}*100/(3.22*10^22)*(daviesIonVelocity[eontd]  /. eontd -> {110.
```

Out[70]= $\{7.53314\times10^{-19},\ 1.61348\times10^{-18},\ 2.72055\times10^{-18}\}$

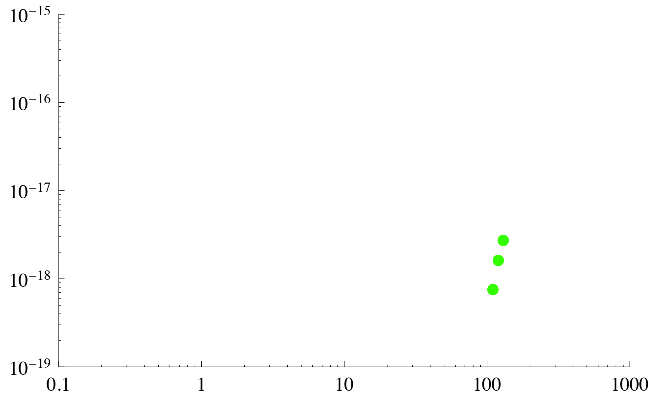
nuon is also symbol for rate coefficient k

In[71]:=
```
nuonDetWagnerTable2  = Transpose[{{110.,120.,130.},nuonDetWagner2}]
```

Out[71]= $\{\{110.,\ 7.53314\times10^{-19}\},\ \{120.,\ 1.61348\times10^{-18}\},\ \{130.,\ 2.72055\times10^{-18}\}\}$

In[72]:=
```
wagnerDetPlot2 = ListLogLogPlot[nuonDetWagnerTable2,  PlotRange -> {{0.1,1000},{10^-19,1.01*1
PlotStyle -> {Hue[0.3],PointSize[0.02]}]
```

Out[72]=



■ Verhaart and van der Laan, J. Appl. Phys. 55, 3286 (1984)

These authors measure the short time current pulse followint pulsed laser induced electron emission. Extrapolation of their moist air data to zero moisture yields data in agreement with the data of Wen and Wetzer (1988).

■ Phelps, Gaseous Dielectrics V, ed by Christophorou and Bouldin (Pergamon, New York, 1987), p. 1. and ftp://jila.colorado.edu/collision_data/electron.txt

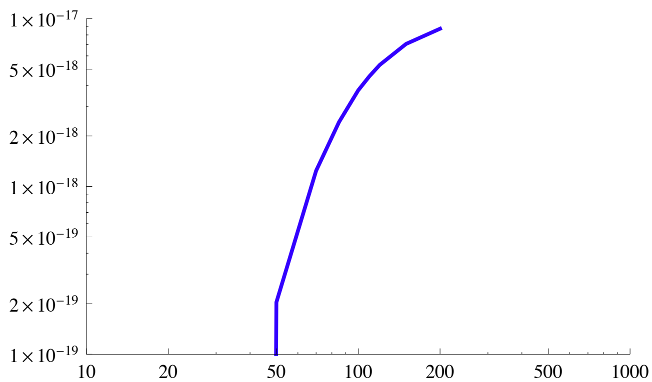
This calculation is based on cross sections for O2 from Lawton and Phelps, J. Chem Phys. 69, 1055 (1978) and for N2 from Phelps and Pitchford, Phys. Rev. 31, 2932 (1985).

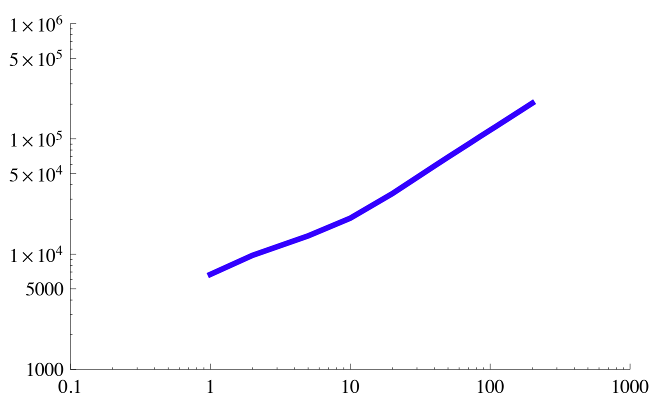
In[73]:=
```
!! dryair.txt
```

```
%Electron transport and reactions in dry air                    3.68E+04    n = 4.00E+14    cm-3 a
From calculations of 2/19/87                Syntax::sntxf: "From digitization of Fig. 14" cannot b
                        effective alph e =      6.00E-05    cm3s-1 at 80 km             s-1
E/n W   Ek  <E> num/m   nuu/n   nu-a3/n^2   nua2/n  nui/n   netnui/n    nua nui netnui  nuu
Td  cm/s    eV  eV  cm3/s   cm3/s   cm6/s   cm3/s   cm3/s   cm3/s   s-1 s-1 s-1 s-1

1.00E-02    4.41E+042.53E-023.78E-02    3.99E-09    ERR ERR ERR ERR ERR ERR ERR ERR ERR
2.00E-02    8.55E+042.61E-023.87E-02    4.11E-09    ERR ERR ERR ERR ERR ERR ERR ERR ERR
5.00E-02    1.80E+053.14E-024.47E-02    4.90E-09    1.66E-11    ERR ERR ERR ERR ERR ERR ERR 6.65E-
1.00E-01    2.49E+054.58E-026.12E-02    7.06E-09    1.26E-11    6.80E-37    1.00E-40    1.00E-40
2.00E-01    2.86E+058.10E-029.93E-02    1.23E-08    1.04E-11    6.90E-37    1.00E-40    1.00E-40
5.00E-01    4.06E+051.48E-011.66E-01    2.17E-08    1.67E-11    3.90E-37    1.00E-40    1.00E-40
1.00E+00    6.15E+052.05E-012.32E-01    2.86E-08    3.44E-11    1.97E-37    1.00E-40    1.00E-40
%The calculations below used improved cross sections
1.00E+00    6.67E+051.94E-012.24E-01    2.64E-08    3.98E-11    1.93E-37    1.00E-40    1.00E-40
2.00E+00    9.76E+052.90E-012.49E-01    3.60E-08    7.39E-11    9.07E-38    1.00E-40    1.00E-40
5.00E+00    1.44E+066.08E-017.24E-01    6.13E-08    1.23E-10    2.89E-38    1.00E-40    1.00E-40
1.00E+01    2.05E+069.12E-019.35E-01    8.58E-08    2.31E-10    1.29E-38    1.00E-40    1.00E-40
2.00E+01    3.35E+061.13E+001.04E+00    1.05E-07    6.05E-10    6.40E-39    1.00E-40    1.00E-40
4.00E+01    5.82E+061.30E+001.14E+00    1.21E-07    1.83E-09    3.48E-39    1.00E-40    1.00E-40
5.00E+01    6.94E+061.37E+001.22E+00    1.27E-07    2.58E-09    1.00E-40    2.04E-13    2.24E-15
7.00E+01    9.01E+061.61E+001.64E+00    1.37E-07    3.97E-09    1.00E-40    1.24E-12    9.49E-14
8.50E+01    1.05E+071.87E+002.10E+00    1.43E-07    4.82E-09    1.00E-40    2.42E-12    5.18E-13
1.00E+02    1.19E+072.16E+002.60E+00    1.48E-07    5.58E-09    1.00E-40    3.74E-12    1.81E-12
1.10E+02    1.28E+072.36E+002.94E+00    1.51E-07    6.04E-09    1.00E-40    4.54E-12    3.49E-12
1.20E+02    1.37E+072.56E+003.28E+00    1.54E-07    6.49E-09    1.00E-40    5.30E-12    6.16E-12
1.50E+02    1.63E+073.13E+004.20E+00    1.62E-07    7.88E-09    1.00E-40    7.07E-12    2.27E-11
2.00E+02    2.04E+073.88E+005.35E+00    1.72E-07    1.06E-08    1.00E-40    8.71E-12    9.43E-11
```

Read in the data from this file and prepare plots.

In[74]:=
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\dryair.txt";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
data2 = Transpose[data1];
attachmentData= Transpose[{data2[[1]],data2[[8]]/10^6}];
driftVelData= Transpose[{data2[[1]],data2[[2]]/100}];
phelpsAttPlot = ListLogLogPlot[attachmentData,PlotRange -> {{10.,1000},{10^-19,10^-17}}, PlotStyle -> {Hu
                    Joined -> True, DisplayFunction->Identity]
phelpsVelPlot = ListLogLogPlot[driftVelData,PlotRange -> {{0.1,1000},{10^3,10^6}}, PlotStyle -> {Hue[0.7],T
                    Joined -> True, DisplayFunction->Identity]
```

Out[83]=


Out[84]=


In[85]:= `phelpsAttInt = Interpolation[attachmentData]`

Out[85]= `InterpolatingFunction[{{1., 200.}}, <>]`

From a fit to the drift velocity data of this file we get

In[86]:= `wFit = 7.*10^3*eontd^0.45*(1+(eontd/13)^2)^0.18;`

■ Wen and Wetzer, IEEE Trans. on Electrical Insulation 23, 999 (1988)

Discharge parameters: 100 < E/n < 110 Td, p20 = 750 Torr, d < 1 cm.
These authors measure the short time current pulse following pulsed laser induced electron emission for dry air. They find the total negative ion loss rate coefficient of <(delta + beta)/p> = 4.8E-3 cm^-1Torr^-1 and the product of the detachment and attachment coefficients of <eta*delta/p^2> = 13E-6 cm^-2Torr^-2. Note that the all of the corresponding rate coefficients are obtained by multiplying by the electron drift velocity.

The sum of their O- loss coefficients is

```
In[87]:= wenIonLoss = {0.0055,0.0051}  (*cm^-1Torr^-1*)

Out[87]= {0.0055, 0.0051}
```

```
In[88]:= daviesIonMobility[eontd] /. eontd -> {100,110}

Out[88]= daviesIonMobility[{100, 110}]
```

```
In[89]:= wenIonLoss2 = wenIonLoss*100/(3.3*10^22)*(wFit /. eontd -> {100,110})  (*cm^3s-1*)
```

Out[89]= $\{1.93748 \times 10^{-18}, 1.93976 \times 10^{-18}\}$

For comparison we add our fits to Frommhold's (1964) detachment coefficient and Parkes' (1974) charge transfer coefficient

```
In[90]:= (deltadeton + kIon2body) /. eontd -> {100,110}
```

Out[90]= $\{1.46465 \times 10^{-18}, 3.37702 \times 10^{-18}\}$

This is rough agreement in magnitude, but the experimental variation with E/n is much too small.

The product of their attachment and detachment coefficients is

```
In[91]:= wenIonProduct = {12.*10^-6, 15.*10^-6}  (*cm^-2Torr^-2*)

Out[91]= {0.000012, 0.000015}
```

```
In[92]:= wenIonProduct2 = wenIonProduct*(100/(3.3*10^22))^2*(wFit /. eontd -> {100,110})^2  (*cm^6s-2
```

Out[92]= $\{1.48912 \times 10^{-36}, 2.16993 \times 10^{-36}\}$

For comparison we add our fits to Phelps' (1987) attachment coefficient and Frommhold's (1964) detachment coefficient

```
In[93]:= (deltadeton /. eontd -> {100,110}) *phelpsAttInt[{100,110}]
```

Out[93]= $\{8.62253 \times 10^{-37}, 2.63363 \times 10^{-36}\}$

The agreement is not good, but not too bad.

■ Teich, Gaseous Dielectrics VI, ed by Christophorou and Sauers (Plenum, New York, 1991), p. 215

Formulation and example of theoretical flux and density waveforms for oxygen at low and at high E/n. No new experimental results.

■ Pasko, Inan, Bell, and Taranko, J. Geophys. Res. 102, 4529 (1997)

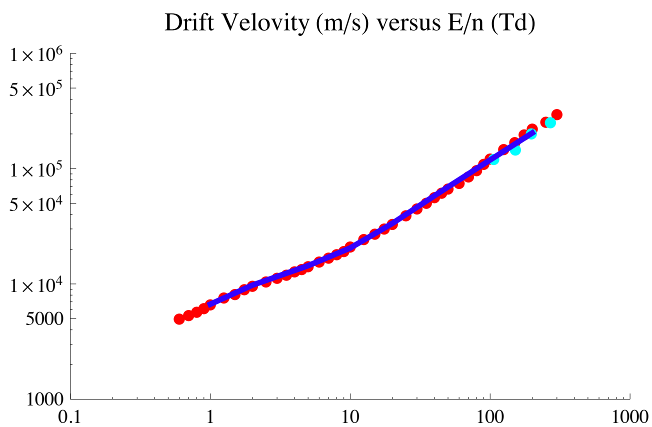
In Fig. 29c the present results for ionization and attachment coefficients that essesntially repeats Phelps (1987). From their comparisons with Davies, I presome they agree with Phelps (1987). Pasko has written later papers on electrons in air at high altitudes - mostly streamer effects.

Plots of transport, attachment, and detachment coefficients

■ Electron Drift Velocity

In[94]:=
```
Show[daviesElectronVelPlot, frommholdVelPlot, phelpsVelPlot, PlotLabel->"Drift Velovity (m/s
```

Out[94]=

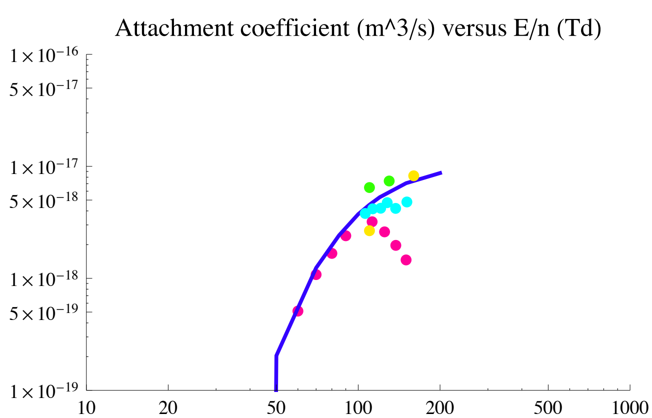


dark blue - Phelps (1987); red - Davies (1983); light blue - Frommhold (1964); green - Wagner (1971); orange - Ruzko (1967)

■ Attachment rate coefficient

In[95]:=
```
Show[daviesAttPlot,phelpsAttPlot,frommholdAttPlot,wagnerAttPlot,  ryzkoAttPlot,
PlotLabel->"Attachment coefficient (m^3/s) versus E/n (Td)"]
```

Out[95]=



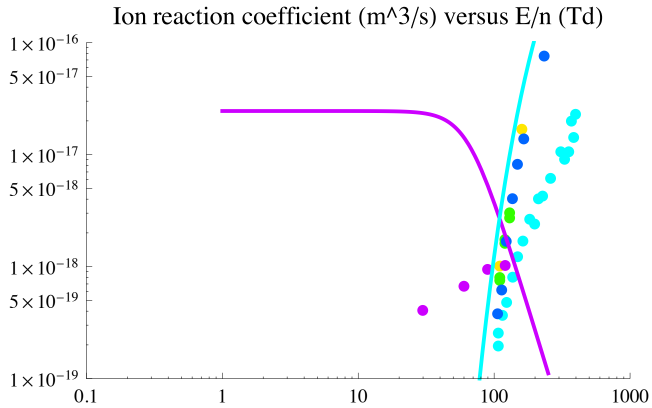
dark blue - Phelps (1987); red - Davies (1983); light blue - Frommhold (1964); green - Wagner (1971); orange - Ruzko (1967)

■ Detachment, charge transfer, and 3-body rate coefficients for O-

I should show energy relaxation rate coefficient.

In[96]:=
```
Show[(*frommholdDetPlot,*) ryzkoDetPlot, raymentDetPlot, goodsonDetPlot,
 wagnerDetPlot1, wagnerDetPlot2, frommholdDetPlot2, parkes3bodyPlot, parkes2bodyPlot,
 PlotLabel-> "Ion reaction coefficient (m^3/s) versus E/n (Td)"]
```

Out[96]=



The points are detachment rate coefficients. The curves are possible O- stabilization reactions. All are in m^3/s.
cyan curve - O- + O2 charge transfer by Parkes (1974); purple curve - O- + 2 O2 -> O3- at 1 atm by Parkes (1974); dark blue points - detachment by O2 from Frommhold (1964); orange points - detachment by O2 from Ryzko (1967); green points - detachment by O2 from Wagner (1971): cyan points - detachment by O2 from Goodson et al (1974); purple points - O- detachment by N2 from Rayment and Moruzzi

Parkes charge transfer needs to be looked at, i.e., it appears to have a threshold at a very critical energy. This behavior is possibly consistent with the detachment cross sections plotted below, but apparently has not been checked by an ion transport/rate coefficient model using Mason et al or MC. See Rebentrost reference.
Why is Goodson and Frommhold low compared to Frommhold?

Beam experiments

▪ Langevin cross section

In this section we consider only the dipole polarizability and neglect the higher multipole polarizabilities.

The value of the mean dipole polarizability for O2 is given by McDaniel and Mason (1980) p. 344 as 1.60 Ang^3 so that in atomic units the polarizability and the Langevin cross section are

In[97]:=
```
ao = 0.529*10^-10;  (*m^2*)
```

In[98]:=
```
alphaauO2 = 1.60 * 10^-30 / ao^3 ;       (*au*)
```

In[99]:=
```
qLangevinO2 =
 2 * Pi * ao^2 * (alphaauO2 / 2 / (enrel / 27.211))^0.5 // PowerExpand      (*m^2 and eV*)
```

Out[99]=
$$\frac{2.13219\times 10^{-19}}{\mathrm{enrel}^{0.5}}$$

In[100]:=
```
langevinO2Plot = LogLogPlot[qLangevinO2, {enrel, 0.01,10}, PlotRange -> {{1.,10}, {3.*10^-22
```

The corresponding ion mobility at NTP from McDaniel (1964), p. 446, is

In[101]:=
```
muLangevinO2  = 35.9 / (alphaauO2 * 32. * 16. / (32. + 16.)) ^0.5  (*cm^2/V-s*)
```

Out[101]= 3.34352

or when normalized to unit density

In[102]:=
```
muNLangevinO2  = 2.69 * 10 ^ 19 * 35.9 / (alphaauO2 * 32. * 16. / (32. + 16.)) ^0.5
```

Out[102]= 8.99406×10^{19}

The Langevin collision frequency is

In[103]:=
```
nuonLangevinO2 = 1.602*10^-19/(1.660*10^-27*16.*32./(16.+32.))/(muNLangevinO2*100)    (*m^3/s
```

Out[103]= 1.00593×10^{-15}

The value of the mean dipole polarizability for N2 is given by McDaniel and Mason (1980) p. 344 as 1.76 Ang^3 so that in atomic units the polarizability and the Langevin cross section are

In[104]:=
```
alphaauN2 = 1.76*1/(10^30*ao^3);
```

In[105]:=
```
qLangevinN2 = PowerExpand[2*Pi*ao^2*(alphaauN2/2/(enrel/27.211))^0.5]
```

Out[105]= $\frac{2.23625 \times 10^{-19}}{\text{enrel}^{0.5}}$

In[106]:=
```
langevinN2Plot = LogLogPlot[qLangevinN2, {enrel, 0.01,10}, PlotRange -> {{1.,10},{3.*10^-22.
 PlotStyle -> {Hue[0.5],Thickness[0.007]}, DisplayFunction->Identity];
```

The corresponding ion mobility at NTP from McDaniel (1964), p. 446, is

In[107]:=
```
muLangevinN2 = 35.9/(alphaauN2*32.*16./(32.  + 16.))^0.5
```

Out[107]= 3.18792

or when normalized to unit density

In[108]:=
```
muNLangevinN2 = 2.69*10^19*35.9/(alphaauN2*32.*16./(32.  + 16.))^0.5
```

Out[108]= 8.5755×10^{19}

The Langevin collision frequency is

In[109]:=
```
nuonLangevinN2 = 1.602*10^-19/(1.660*10^-27*16.*32./(16.+32.))/(muNLangevinN2*100)   (*m^3/s
```

Out[109]= 1.05503×10^{-15}

- **Muschlitz, IV Int. Conf. Ionization Phenomena in Gases, Uppsula (North Holland, Ammsterdam,1960) p 52**

- **Chantry and Schulz, Phys. Rev. 156, 134 (1967)**

Measure energy distribution of O- formed by dissociative attachment of electrons to O2 for various incident electron energies.

- **Roche and Goodyear, J. Phys. B 2, 191 (1969)**

- **Bailey and Mahadavan, J. Chem. Phys. 52, 179 (1970)**

- **Ranjan and Goodyear, J. Phys. B 6, 1070 (1973)**

- **Comer and Schulz, Phys. Rev. A 10, 2100 (1974)**

- **O- + O2 plot**

In[110]:=
```
!!Comer74.dat
```

```
%Detachment cross section for O- + N2 collisions
Fig. 3 of Comer and Schulz, Phys. Rev. A 10, 2100 (1974)
   %Erel (eV) Qct (m^2)
   0.3906     6.122e-21
   0.5078     4.247e-21
   0.7031     2.946e-21
   0.8203     2.181e-21
   0.9766     1.798e-21
   1.1328     1.4541e-21
   1.3281     1.2245e-21
   1.641      9.566e-22
   1.953      9.184e-22
   2.227      9.566e-22
   2.617      1.1097e-21
   3.203      1.5306e-21
   3.867      2.219e-21
   4.453      3.176e-21
   5.117      4.439e-21
   5.742      5.855e-21
   6.328      7.347e-21
   6.953      8.648e-21
   7.578      9.49e-21
   8.203      9.949e-21
   8.867      1.0293e-20
   9.492      1.0485e-20
   10.117     1.0791e-20
   10.781     1.1288e-20
   11.445     1.1862e-20
   12.07      1.2321e-20
   12.695     1.301e-20
   13.32      1.389e-20
   13.984     1.4503e-20
   14.609     1.5268e-20
```

Read in the data from this file and prepare plots of O- detachment in collisions with N2

In[111]:=
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\Comer74.dat";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
comerN2DetPlot =ListLogLogPlot[data1,PlotRange -> {{0.1,1000},{3.*10^-22,3.*10^-19}}, PlotStyle -> {Hue[0
                    DisplayFunction->Identity];
```

- **O- + N2 plot**

In[118]:= `!!Comer74O2.dat`

```
%Detachment cross section for O- + O2 collisions
Fig. 2 of Comer and Schulz, Phys. Rev. A 10, 2100 (1974)
   %Erel (eV) Qct (m^2)
   1.0247     7.289e-22
   1.693      2.551e-21
   2.495      4.92e-21
   3.119      6.743e-21
   3.832      8.383e-21
   4.812      1.0023e-20
   6.193      1.1298e-20
   7.084      1.221e-20
   8.109      1.3121e-20
   9.134      1.385e-20
   10.649     1.3667e-20
   11.985     1.4396e-20
   13.099     1.5307e-20
   14.436     1.64e-20
   15.46      1.822e-20
   16.66      2.114e-20
```

Read in the data from this file and prepare plots of O- detachment in collisions with N2

In[119]:=
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\Comer74O2.dat";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
comerO2DetPlot =ListLogLogPlot[data1,PlotRange -> {{0.1,1000},{3.*10^-22,3.*10^-19}}, PlotStyle -> {Hue[0
                    DisplayFunction->Identity];
```

- **Vogt, Dreves, and Mischke, Z. Naturforsch. 32a, 13 (1977)**

In[126]:= `!!Vogt77.dat`

```
%Charge transfer cross section for O- + O2 collisions
Fig. 1 of Vogt et al, Z. Naturforsch. 32a, 13 (1977)
   %Erel (eV) Qct (m^2)
   0.9859     4.906e-22
   1.112      8.302e-22
   1.238      1.2736e-21
   1.3641     1.4623e-21
   1.742      1.896e-21
   1.4902     1.991e-21
   1.868      2.123e-21
   2.625      2.34e-21
   2.121      2.396e-21
   2.373      2.594e-21
   2.877      2.613e-21
   3.382      2.679e-21
   3.255      2.783e-21
   3.634      2.811e-21
   4.012      2.708e-21
   4.264      2.651e-21
   4.516      2.509e-21
   4.895      2.434e-21
   5.273      2.189e-21
   5.903      1.896e-21
   6.786      1.849e-21
   6.408      1.698e-21
   7.542      1.4906e-21
   8.299      1.2547e-21
   8.425      1.0755e-21
   9.812      7.547e-22
   10.947     4.811e-22
   12.334     3.962e-22
   13.469     3.774e-22
   15.86      4.151e-22
   18.26      4.623e-22
   21.29      5.566e-22
   23.18      6.226e-22
   27.34      8.208e-22
   31.5       1.0566e-21
   33.39      9.528e-22
   35.41      1.1415e-21
   37.43      1.0566e-21
   41.46      1.3208e-21
   43.73      1.4623e-21
   45.62      1.4245e-21
   47.64      1.774e-21
   49.53      1.858e-21
   55.96      2.057e-21
   57.73      2.217e-21
   59.87      2.283e-21
   61.76      2.406e-21
   63.9       2.651e-21
   66.68      2.575e-21
   69.58      2.368e-21
```

Read in the data from this file and prepare plots of O- + O2 -> O2- + O

In[127]:=
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\Vogt77.dat";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
vogtCTPlot = ListLogLogPlot[data1,PlotRange -> {{0.1,1000},{3.*10^-22.,3.*10^-19}}, PlotStyle -> {Hue[0.8],P
                        DisplayFunction->Identity];
```

■ Penent et al, J. Phys. B 20, 6065 (1987)

Electron detachment cross section for O- with N2

In[134]:=

```
!!Penent87.dat
```

```
%Electron detachment cross section in O- + N2 collisions
Fig. 4 of Penent et al, J. Phys. B 20, 6965 (1987)
   %Erel (eV) Qdet (m^2)
   6.746      1.593e-20
   6.934      1.698e-20
   7.462      2.063e-20
   8.406      2.69e-20
   9.824      3.108e-20
   11.91      3.761e-20
   15.396     3.996e-20
   20.46      4.728e-20
   25.97      5.015e-20
   31.48      5.25e-20
   37.13      5.616e-20
   42.21      5.72e-20
   47.99      6.007e-20
   54.57      5.903e-20
   59.81      5.981e-20
   71.19      6.086e-20
   82.44      6.164e-20
   93.73      6.399e-20
   104.63     6.399e-20
   121.16     6.582e-20
   137.76     6.582e-20
   158.07     6.582e-20
   184.7      6.504e-20
   213.9      6.373e-20
   245.5      6.399e-20
```

Read in the data from this file and prepare plots of O- detachment in collisions with N2

In[135]:=

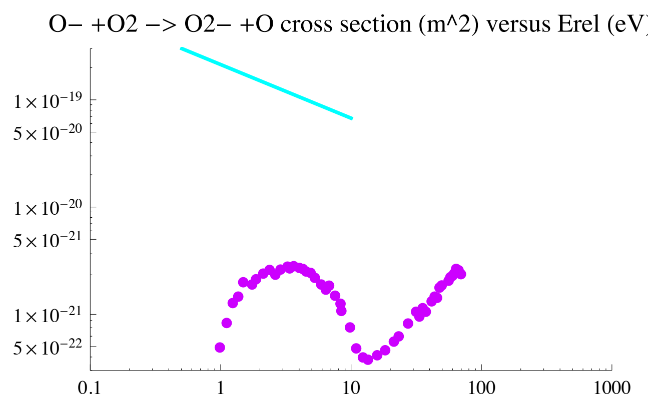
```
inputfile := "c:\\users\\avp\\documents\\mathbook\\air\\attachmentdetachment\\Penent87.dat";
stream = OpenRead[inputfile];
Find[stream,"%"];
Find[stream,"%"];
data1 = ReadList[stream, Number,RecordLists ->True];
Close[stream];
penentDetPlot =ListLogLogPlot[data1,PlotRange -> {{0.1,1000},{3.*10^-22,3.*10^-19}}, PlotStyle -> {Hue[1.],I
                              DisplayFunction->Identity];
```

- **O- + O2 -> O2- + O cross section plots**

In[142]:=

```
Show[vogtCTPlot, langevinO2Plot, PlotLabel->"O- +O2 -> O2- +O cross section (m^2) versus Ere
```

Out[142]=

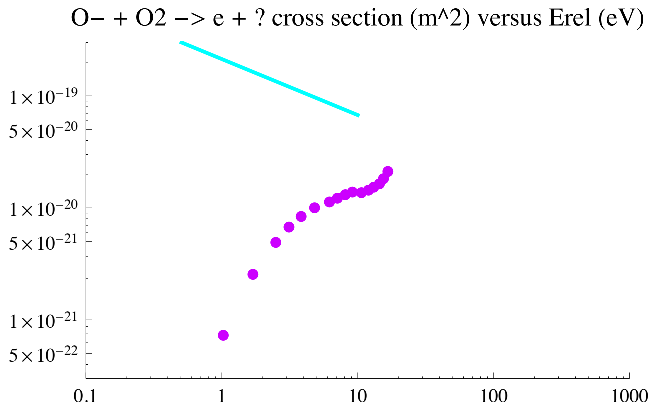


cyan curve - Langevin; purple points - Vogt et al

O- + O2 -> e + ? cross section plots

In[143]:=
```
Show[comerO2DetPlot, langevinO2Plot, PlotLabel->"O- + O2 -> e + ? cross section (m^2) versus
```

Out[143]=

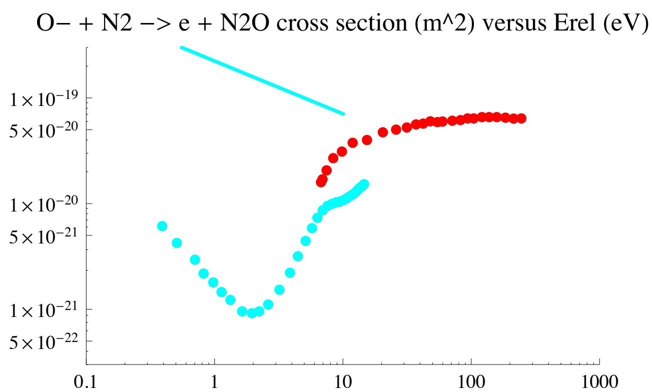


cyan curve - Langevin; purple points - Comer et al

- **O- + N2 -> e + N2O cross section plots**

In[144]:=
```
Show[comerN2DetPlot,penentDetPlot, langevinN2Plot, PlotLabel-> "O- + N2 -> e + N2O cross sec
```

Out[144]=



cyan curve - Langevin; cyan points - Comer et al; red points - Penent et al (1987)

Reaction energies

- **Consider O- + O3 -> 2 O2 + e and O- + O2 -> e + O3**

The energy required is found using the following procedure borrowed from our METHANESPATIAL.NB model. The enrgies are from NIST WebBook except for O3 dissociation from Mauer and Schulz (1973). The WebBook gives 2.95 eV, but for what? 2*O3 -> 3*O2?

- **Energies without CO2, etc.**

```
do2 = 5.17; eao = 1.46; eao2 = 0.45; do3 = 1.07; eao3 = 2.10;
```

In order to get what I understand the NIST WebBook to give we need to use do3 = 1.11 eV

```
do2 = 5.17; eao = 1.46; eao2 = 0.45; do3 = 1.11; eao3 = 2.10;
```

```
equations = {o2 == 2 * o + do2, on == o + e + eao,
   o2n == o2 + e + eao2, o3 == o2 + o + do3, o3n == o3 + e + eao3;};
```

```
variables = {e, o, o2, o3, o2n, o3n, on};
```

- **Energies with CO2, etc.**

In the following, we are still trying to find better data for the C containing species, i.e., the CO-O bond and especially the CO2-O-bond.

```
In[145]:= do2 = 5.17; eao = 1.46; eao2 = 0.45; do3 = 1.07; eao3 = 2.10;
          eaco3 = 3.34; dco3 = 0.39; dco3n = 1.97; dco2 = 5.44; dco = 11.11;
```

```
equations = {o2 == 2 * o + do2, on == o + e + eao, o2n == o2 + e + eao2, o3 == o2 + o + do3,
   o3n == o3 + e + eao3, co3n == co2 + on + dco3n, co2 == co + o + dco2, co == c + o + dco};
```

```
In[146]:= equations = {o2 == 2 * o + do2, on == o + e + eao, o2n == o2 + e + eao2,
            o3 == o2 + o + do3, o3n == o3 + e + eao3, co3n == co2 + on + dco3n, co2 == co + o + dco2};
```

```
In[147]:= variables = {e, o, o2, o3, o2n, o3n, on, co2, co3n, co, c};
```

- **Reaction energies**

For the O- + O3 -> O3- + O reaction

```
In[148]:= Eliminate[Join[{d == co3n + co - (2 co2 + e)}, equations], variables]
Out[148]= d == -2.01
```

For the O- + O3 -> O3- + O reaction

```
In[149]:= Eliminate[Join[{d == on + o2 - (o2n + o)}, equations], variables]
Out[149]= d == 1.01
```

For the O- + O3 -> 2 O2 + e   reaction

```
In[150]:= Eliminate[Join[{d == on + o3 - (2 * o2 + e)}, equations], variables]
Out[150]= d == -2.64
```

As a check on the sign consider O- -> O + e

```
In[151]:= Eliminate[Join[{d == on - (o + e)}, equations], variables]
Out[151]= d == 1.46
```

For the O- + O2 -> O3 + e reaction

```
In[152]:= Eliminate[Join[{d == on + o2 - (o3 + e)}, equations], variables]
Out[152]= d == 0.39
```

The following does not work for reasons I do not understand: For the O- + O3 -> O3- + O reaction

```
Eliminate[Join[{d == on + o3 - (o + o3n)}, equations], variables]
```

The reaction should be exothermic by 0.64 eV, and we get the solution using Solve[].

In[153]:=
```
Solve[Join[{d == +on + o3 - (o3n + o)}, equations], d, variables]
```
Out[153]= {{d → -0.64}}

In[154]:=
```
Solve[Join[{d == 3 * o2 - 2 * o3 }, equations], d, variables]
```
Out[154]= {{d → 3.03}}

In[155]:=
```
Solve[Join[{d == o3 - (o2 + o) }, equations], d, variables]
```
Out[155]= {{d → 1.07}}

In[156]:=
```
Solve[Join[{d == o3n + o3 - (3 * o2 + e) }, equations], d, variables]
```
Out[156]= {{d → -0.93}}

Summary

Initial attachment and ion collision processes

In this section we are concerned with the choice of a model of the initial attachment and detachment processes in O2 and in dry air. The O- formed by dissociative attachment of an electron with O2 is subject to several possible ion-molecule reactions as it relaxes in energy toward a steady-state energy distribution and as it is destroyed by collisions. These reactions include electron detachment in collisions with O2 and N2, charge transfer collisions with O2, and three-body reactions with an O2 and with a third body, i.e., O2 or N2, to form O3-. On a longer time scale, one may have to include O- production by collisional dissociation of O3-, etc.

Frommhold and coworkers (1974) discuss a model in which one regards the initial attachment and ion reaction sequence as an effective attachment process leading to the formation of O2- and O3-. Such a model is appropriate when the O- reactions occur on a time scale comparable with the O- energy relaxation time. A disadvantage of this approach is that one ends up with very odd pressure dependencies for the effective attachment coefficients, especially when three-body formation of O3- is included.

The initial attachment and ion collision processes in O2 have been modeled using Monte Carlo techniques by Okada et al (1978). They neglect the three-body formation of O3-. They find that for E/n = 141 Td about 6 collisions are required for the O- to reach a steady-state energy distribution, i.e., about 6/(6e-10*N) sec (~300 ns at 1 Torr and ~0.4 ns at 1 atm pressure), while the e-folding decay of O- number requires about 50 collisions (~ 2 us at 1 Torr). I conclude that, this relative long decay time for the O- population would seem to show that the rate equation approach should work. (Okada et al (1978) do not make a recommendation). This result is dependent on the relatively low ratio of the cross sections for O- + O2 reactions to the elastic (Langevin) cross section at the energies of the O- ions formed by dissociative attachment, i.e., at <Elab> ~ 1.5 eV Lab or <Ecm> = ~1 eV,. Note that this large ratio of elastic to reaction cross sections does not hold for higher energy O- collisions, e.g., > 10 eV in center of mass.

The situation is less clear for the modeling of electron and negative ion behavior in air. Depending on which experiment one accepts for O- detachment in collisions with N2, the cross section ratio may be less favorable for the rate equation approach for air than for O2. See Comer and Schulz (1974) versus Lindinger et al (1975).

Cross sections for collisions of electrons and photons with atomic oxygen
Itikawa,Y.(Inst.of Space& Astronaut.Sci.,Sagamihara,Japan);Ichimura,A.Source:Journal of Physical and Chemical Reference Data,v 19,n 3,May-June 1990,p 637-51

In[157]:=
```
Quit[]
```