A DETERMINATION OF THE CONCENTRATION RANGE
AT WHICH No, NEUTRALIZES Pb-218 IONS

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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I greatly appreciate Dr. V. Leong for giving me the opportunity to work with these chemically rare named daughter and for having the patience and the insight to manage my inquisitive nature. I also appreciate S. Goldstein for being such an experimental wizard and for his ingenious experimental setup. I would also like to thank him for his wonderful sense of humor which turned some of the most difficult times into pleasant experiences. Finally, special thanks are due to Dr. V. Leong who enthusiastically assisted S. Goldstein and me whenever we consulted him.
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In the past decade, the chemistry of radioactive isotopes has become more and more a topic of study. One such element that has captured scientific attention is Po-218 and its ions. The chemistry of Po-218 and other Rn-222 daughters (Fig. 1) originally was pursued in order to control airborne radioactive Rn-222 and its daughters in U-238 mines (1). Yet the uses of Rn daughter studies have spread to meteorology(2) and human biology(2).

Rn daughter chemistry, though, is difficult to investigate because the short half-lives of Rn daughters require excessive amounts of Ra-226 in order to produce high enough concentrations of daughters so that they can be examined spectroscopically. Therefore, if one wants to use a moderate level of Ra-226 as a source, the chemistry of Rn daughters can only be investigated by indirect means. One such indirect method is the experimental observation of the molecular diffusion coefficient of these daughters, both charged and neutral, in various gases of varying concentrations(1).
The diffusion coefficient is the negative of the proportionality constant between a component's molecular flux and its concentration gradient under constant total pressure (3):

\[ J_n = -D \frac{\partial (N_n/V)}{\partial z} \]  

\[ J_n \] = molecular flux in the z direction (molecules/cm² s)
\[ N_n \] = number of molecules of species n
\[ V \] = box volume (cm³)

Let there be a box with \( N \) molecules of gas(1) located in a box with other gases. This box is located in a \((x,y,z)\) Cartesian coordinate system. If the concentration gradient in the z direction is small, but if gas(1) quickly diffuses into the other gases, one can see from equation [1] that \( D \) is obviously large. In turn, \( D \) is small whenever a large concentration gradient is not accompanied by a comparatively large flux (3).

\[ D \] is also pressure and temperature dependent. For an ideal gas, \( D \) decreases with increasing pressure and increases with increasing temperature (3).

\[ D = \frac{\nu}{2} \]
In order to use the two filter method developed by Fantan(5) and Jacobi(6), Rn-222 gas must be produced in sufficient quantities. It is generated by bubbling an inert gas, $N_2$ for example, through a water solution of $Ra(226)Cl_2$. This Rn gas stream then merges with an experimental gas stream, whose effect on Rn daughters one wants to study. This merged stream then proceeds to a diffusion tube cylinder. At the inlet port of the tube a glass fiber filter absorbs any Rn daughters that may have formed in transit to the tube and allows all gases including Rn to pass through it. The Rn gas then decays within.
This two filter method eliminates the need for a calibration of the inlet Rn concentration. Without the inlet filter, one must calibrate an unknown RnCl₂ source to a known one by comparing the exit filter count totals of both sources. Yet the inlet filter, that prevents the daughters from entering the tube, exactly sets the volume in which daughters can form. This volume is simply the volume of the diffusion tube itself.

Taylor and Lucas(7) attempted to use the Gurnley-Kennedy(8) equation to estimate $F_f$, the fraction of Rn daughters that do not diffuse to the tube wall. Yet this equation does not take into account Rn daughters that form within the tube volume. Therefore, it does not apply for the two filter method. Consequently, Tan(9) derived an equation of the Rn concentration as a function of $F_f$ while considering only the daughters that form within the tube.
II. Theory

A. Inlet Rn Concentration

One must find an equation of $C_1$, the inlet Rn concentration, in terms of known experimental parameters. Probably the best way to express this inlet Rn concentration is in terms of the amount of Po-218 created per unit time-volume (2):

$$C_1 = \sqrt[4]{Q_1/2}$$  \hspace{1cm} [4]

$$T = \sqrt[4]{Q_1 \text{, V}}$$ \hspace{1cm} [5]

$$C_1 = 0.45 \left( \frac{Q_1}{A} \right)$$ \hspace{1cm} [6]

Since $T$ cannot be directly measured, a factor with the same dimensional units can be substituted (2):

$$T = \frac{X}{EZ}$$ \hspace{1cm} [7]

$$C_1 = 0.45 \left( \frac{X}{EZV} \right)$$ \hspace{1cm} [8]
subscripts:

\( n = 0: \text{Ra-226} \)
\( n = 1: \text{Rn-222} \)
\( n = 2: \text{Po-218 (RaA)} \)
\( n = 3: \text{Pb-214 (RaB)} \)
\( n = 4: \text{Bi-214 (RaC)} \)

\( C_1 = \) inlet Rn concentration (pCi/liter)
\( X = \) number of counts detected between \( T_1 \) and \( T_2 \)
\( \lambda_n = \) decay constant (m\(^{-1}\))
\( V = \) diffusion tube volume (liters)
\( Q_n = \) concentration of species \( n \) (molecules/liter)
\( I = \) rate of Rn daughter arrival at exit filter (molecules/m)
\( E = \) counter's counting efficiency
\( Z = \) a constant of the buildup and the decay process (m)

In equation (8), \( C_1 \) is expressed in terms of variables either that can be measured experimentally or that can be calculated from experimental parameters. For instance, \( X, E, \) and \( V \) can be measured directly. Both \( Z \) and \( F_f \), though, are complicated functions of several experimental parameters. \( Z \) is a constant of the buildup and the decay process and is a function of \( t, T_1, \) and \( T_2 \) where \( t = \) integrated buildup time(m) and where \( T_m = \) Bateman decay time(m). \( F_f \) is a non-explicit function of \( Q_x, D, \) and \( L \) where \( L = \) diffusion tube length(cm). Since \( C_1 \) is always constant, one must choose a \( D \) such that as \( X \) rises with increasing \( Q_x \), \( F_f \) rises proportionately.
B. Calculation of $Z$

A function for $Z$ can be explicitly evaluated by considering an integrated buildup on the exit filter for time, $t$, followed by a Bateman type decay(2). This decay starts at $T_m = 0$, but it is detected by a counter between $T_m = T_1$ and $T_m = T_2$. The only decay equations that are considered in the $Z$ function involve alpha decay since the proportional counter is geared to only detect alpha decay, but all of these equations through the one for RaC are considered. Since the half-life of RaC is so short, its decay equation is identical to the one for RaC.

Since $F_f$ corrects $C_1$ for the daughters that diffuse to the tube wall, the daughter concentration at the exit port must be less than $C_1$ by a factor of $F_f$. Also if one assumes that Po-218 decay within the tube volume is negligible so that only traces of Pb-214 and Bi-214 reach the exit port, then:

$$q_f = 0, \quad r_1 = q_f$$

$q = \text{flow rate in the diffusion tube (liters/m)}$

The following rate equations describe the buildup of isotopes on the exit filter:

$$\frac{dN_2}{dt} = -\lambda_2 N_2$$
These equations can then be solved consecutively to yield the following solutions:

\[ N_2^* = \left( \frac{1}{\lambda_2} \right) (1 - e^{-\lambda_2 t}) \]  

\[ N_1^* = \left( \frac{1}{\lambda_1} \right) \left[ (1 - e^{-\lambda_1 t}) - \left( \frac{\lambda_1}{\lambda_2 - \lambda_1} \right) (e^{-\lambda_2 t} - e^{-\lambda_1 t}) \right] \]  

\[ N_0^* = \left( \frac{1}{\lambda_0} \right) \left[ (1 - e^{-\lambda_0 t}) - \left( \frac{\lambda_0}{\lambda_1 - \lambda_0} \right) (e^{-\lambda_1 t} - e^{-\lambda_0 t}) - \left( \frac{\lambda_0}{\lambda_2 - \lambda_0} \right) (e^{-\lambda_2 t} - e^{-\lambda_0 t}) + \left( \frac{\lambda_0}{\lambda_3 - \lambda_0} \right) (e^{-\lambda_3 t} - e^{-\lambda_0 t}) \right] \]

\[ \mathbf{N}_n^* = \text{number of nuclei of isotope } n \text{ at } T_m = 0 \]

After a daughter build up during time, \( t \), the Rn gas flow is diverted away from the diffusion tube, and the decay of daughters on the filter paper proceeds in a Bateman manner(10) starting at \( T_m = 0 \). Replacing \( T_m \) with \( T \) for the following equations only, an equation for \( Z \) can be calculated.

\[ \mathbf{N}_n = \sum_{i=1}^{n} \sum_{i=1}^{n} C_{i,k} e^{-\lambda_i t} \cdot \mathbf{C}_{m,n} = \left[ 1, \ldots, N_{n-1}^* \right] \frac{1 - N_n^*}{(\lambda_1 - \lambda_m) \ldots (\lambda_{n-1} - \lambda_m)} \cdot \left[ 1, \ldots, (\lambda_{n-1} - \lambda_m) \right] \]
If only the alpha decays of RaA and RaC' are considered, the activity, \( A_c \), at time, \( T \), can be expressed like so (2):

\[
A_c(T) = \lambda_2 N_2 + \lambda_4 N_4.
\]  

[17]

Since the total number of counts that the counter detects between \( T_1 \) and \( T_2 \) is \( X/E \), then:

\[
X/E = \frac{\int_{T_1}^{T_2} A_c(T) \, dT}{T_2 - T_1} = g(t, T_1, T_2).
\]  

[18]

Yet:

\[
z = X/E; \quad z = g(t, T_1, T_2)
\]  

[19]

Different values of \( t, T_1, \) and \( T_2 \) can be plugged into \( g(t, T_1, T_2) \) to yield different values of \( z \) (1, 4).

C. \( F_f \) Determination

If \( \mu = (\pi)D^mL/Q_g \), \( F_f \) can be expressed as a very complex function of \( \mu \), derived by Tan(12), that can most easily be expressed in implicit tabular form(2). Since \( F_f \) is inversely related to \( \mu \), as one would expect, \( F_f \) decreases with \( D \) and \( L \), but it increases with \( Q_g(2) \).
In this diffusion tube experiment at low flow rates when \( \mu > 0.34 \), a parabolic velocity distribution is assumed to develop in the tube. Yet as the flow rates get higher and when \( \mu < 0.34 \), a Langhaar velocity profile, that is a combination of a parabolic and a uniform distribution, is assumed for the \( \mu \) versus \( F_r \) calculation (1).
III. Neutralization Mechanisms

A. Introduction

When Rn-222 gas emits an alpha particle, Po-218, its daughter is positively charged at its time of birth 88% of the time (11). The other 12% of these Po-218 daughters are born neutral (11). Since positively charged molecules usually cluster with other molecules, Po⁺ has a lower diffusion coefficient than its neutral counterpart. This lower D value results because Po⁺ clusters are more massive than the individual Po atoms (1).

If \( D_n \) is the diffusion coefficient of a neutral molecule, a calculation of \( D_n \) for neutral Po-218 yields a value equal to \( 0.041 \) cm²/s in \( N_2 \) gas at \( P=1 \) atm and \( T=300 \) K (eq. [2], 12). Experimentally derived D values are larger than this calculated value by an approximate factor of two. According to Thomas and LeClare (2), \( D_n = 0.085 \) cm²/s. Yet according to Frey (1), \( D_n = 0.072 \) cm²/s. Therefore, the actual value of \( D_n \) probably falls between these values.

Frey (1) in his paper used the two filter method to investigate the diffusion coefficient of Po-218 in 10 ppm \( N_2 \) in \( N_2 \), in 10 ppm NO in \( N_2 \), in 8.3 ppm NO in 92% \( N_2 \) and 8% \( O_2 \), and in \( N_2 \) with varying degrees of relative humidity. The diffusion coefficient of Po-218 in these gases indicates neutralization takes place in \( N_2 \) with 10ppm \( N_2 \), in \( O_2 \) with NO present, and in 20-80% relative humidity (1, Table 1). Apparently,
<table>
<thead>
<tr>
<th>Experimental Gas in N₂</th>
<th>Diffusion Coefficient (cm²/s)</th>
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<tbody>
<tr>
<td>N₂ (dry)</td>
<td>0.037 ± 0.0003</td>
</tr>
<tr>
<td>97% O₂ (dry)</td>
<td>0.030 ± 0.0006</td>
</tr>
<tr>
<td>10 ppm NO (dry)</td>
<td>0.032 ± 0.0006</td>
</tr>
<tr>
<td>10 ppm NO₂ (dry)</td>
<td>0.072 ± 0.0004</td>
</tr>
<tr>
<td>10 ppm C₂H₄ (dry)</td>
<td>0.032 ± 0.0005</td>
</tr>
<tr>
<td>8.3 ppm NO (dry) with 8% O₂</td>
<td>0.072 ± 0.0006</td>
</tr>
<tr>
<td>Dry pump air</td>
<td>0.026 ± 0.0013</td>
</tr>
<tr>
<td>20% RH N₂</td>
<td>0.072 ± 0.0008</td>
</tr>
<tr>
<td>80% RH N₂</td>
<td>0.072 ± 0.0004</td>
</tr>
</tbody>
</table>
though, Po-218 can be neutralized by any one of three different mechanisms. In the presence of NO and O₂, Po⁺ ions are neutralized by an electron exchange mechanism. Yet in the presence of H₂O, Po⁺ ions are probably neutralized by an electron scavenging mechanism. A third possibility for a neutralization mechanism involves an atomic exchange, along with an extra electron exchange, from a trace molecule in the carrier gas to the Po⁺ ion. The observation of the neutralization of Po⁺ in NO₂ raises the question of which mechanism brings about this unexpected result. In the first case, the electron exchange mechanism is thermodynamically impossible. Secondly, the atomic exchange mechanism can be efficiently discarded because the time, required for neutralization by this mechanism, is so long that the diffusion coefficient would be unaffected by NO₂'s presence. Therefore, the only acceptable reason for Po⁺ neutralization in 10 ppm NO₂ is that NO₂ is an excellent electron scavenger. Therefore, in order to find out how effective of a scavenger NO₂ actually is, finding the NO₂ concentration, at which Po⁺ is only partially neutralized, is a goal worth pursuing.

R. Electron Exchange Mechanism

In this mechanism an electron is exchanged from one of the trace gas molecules to the Po⁺ ion. Yet this mechanism requires that the ionization potential (IP) of neutral Po or of its neutralized intermediate complex (PoO₂ for example) must be greater than the IP of this trace gas molecule (1, Table II) in order for neutralization to take place. For example, if RaA is diffused in a gas without any
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<th>Experimental Gases</th>
<th>Ionization (a) Potentials(eV)</th>
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<tr>
<td>N₂</td>
<td>15.58</td>
</tr>
<tr>
<td>O₃</td>
<td>12.10</td>
</tr>
<tr>
<td>NO</td>
<td>9.25</td>
</tr>
<tr>
<td>PO₂</td>
<td>10 (a)</td>
</tr>
<tr>
<td>NO₂</td>
<td>9.79</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.56</td>
</tr>
<tr>
<td>Po</td>
<td>8.43</td>
</tr>
</tbody>
</table>

(a) Values obtained from reference (1).
molecular $O_2$, the IP(Po) should be too small to remove an electron from $NO_2$, NO, $H_2O$, or $N_2$. Yet if RaA is diffused in a gas with a considerable amount of $O_2$, a $PoO_2^+$ complex ion forms. This ion now has the required IP to remove an electron from NO or $NO_2$ but not from $H_2O$, $O_2$, or $N_2$.

This mechanism has been verified for trace NO gas, for only in the presence of $O_2$ did NO neutralize Po$^+$. Yet this mechanism cannot explain Po$^+$'s neutralization either in $NO_2$ gas without $O_2$ or in 20-%$O_2$ relative humidity with pure $N_2$.

C. Atomic Exchange Mechanism

Since the IP($NO_2$) is too high for $NO_2$ to give up an electron to Po$^+$, a simple electron exchange cannot take place. Po$^+$, though, could remove one of $NO_2$'s labile oxygens with or without an extra electron in one of the following two ways (15):

1. $Po^+ + NO_2 \rightarrow PoO + NO^+$

2. $Po^+ + 2NO_2 \rightarrow PoO + 2NO$

$PoO_2^+ + NO_2 \rightarrow PoO + NO^+$

One way to determine if either of these reactions is practical, is to determine if either reaction is allowed thermodynamically. For 1 the required feasibility condition is:
BE(Po-O) + IP(Po) > BE(O-NO) + IP(NO₂)

IP = ionization potential (eV)
BE = bond energy (eV)

Since BE(O-NO) = 3.17eV (15), BE(Po-O) > 4.5eV for this reaction to happen spontaneously. Since BE(Te-O) = 4.06eV (14) and since Po is a larger atom than the Te atom, BE(Po-O) is probably less than 4.06eV. Therefore, 1 is thermodynamically impossible.

For 2 the required condition is:

2BE(Po-O) + IP(Po) > 2BE(O-NO) + IP(NO₂)

Therefore, BE(Po-O) must be greater than 3.85eV in order for this reaction to be practical. Since BE(Po-O) can be less than 4.06eV without being smaller than this thermodynamic minimum, reaction 2 is thermodynamically possible.

Even though reaction 2 is thermodynamically allowed, one must see if the reaction is kinetically possible. The best way to find out is to compare the time for effective neutralization (t_rxn) to the maximum reaction time period for which the diffusion coefficient detects total neutralization (t_D). Since total neutralization was observed for a NO₂ concentration of 10ppm, t_rxn at this concentration must be less than t_D in order for reaction 2 and also the atomic exchange mechanism to be
the sought for explanations of reality.

1) *t_D* Assumption

Miller(17) found that at relative humidities to 40-50%, Po+ is effectively neutralized in approximately 4 ms. Yet, according to Thomas and LeClare(2), the Po+ diffusion coefficient detects complete neutralization for all relative humidities greater than 20%. Since the concentration of H_2O at which D detects complete neutralization is one-half of what Miller used to measure *t_fxn* of H_2O, the time sensitivity of D (*t_D*) is 8 ms. Therefore, only a mechanism that neutralizes Po+ in less than 8 ms will result in D = 0.072 cm^2/s, which reflects total neutralization.

2) *t_fxn* Calculation

According to the Arrhenius Activation Law(3), the reaction rate is equal to the collision frequency(*z_f_AB*) of molecules A and B times the probability(*P_y*) that a collision has the minimum activation energy(*E_A*).

\[
 z_f_{AB} = z_f_{AB} \left( \frac{8kT}{\pi a_{AB}} \right) \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right) \]  

\[
 P_y = e^{-\left( \frac{E_A}{kT} \right)} \]
\[ \frac{dx}{dt} = zf_{AB}(Py) \]  

\[ zf_{AB} = \text{collision frequency between A and B (collisions/s)} \]

\[ Py = \text{probability that a collision can overcome the activation energy} \]

\[ E_A = \text{Arrhenius activation energy (eV)} \]

\[ \sigma_{AB} = \text{reaction cross section between A and B (cm}^2) \]

\[ u_{AB} = \text{reduced mass} = \frac{m_A m_B}{(m_A + m_B)} \text{ (kg)} \]

\[ x = \text{concentration of the reactants, lost in reaction (molecules/cm}^3) \]

Since \( N_A/V = L_0[A] \), \( N_B/V = L_0[B] \), and \( x = L_0[x] \):

\[ \frac{d[x]}{dt} = k_2[A][B] \]  

\[ k_2 = \sigma_{AB} \nu_0 (8kT/\pi u_{AB})^{1/2} e^{-\left(\frac{E_A}{kT}\right)} \]  

\[ L_0 = 6.02 \times 10^{23} \text{ molecules/mole} \]

\[ [C] = \text{concentration of C (moles/cm}^3) \]

\[ k_2 = \text{2nd order rate constant (cm}^3/\text{mole} \cdot \text{sec}) \]

If one assumes that the reaction of \( \text{Po}^+ \) with the first \( \text{NO}_2 \) molecule is the probable rate determining step, reaction sequence 2 can be considered as a single second order reaction:
\[
3 \quad \text{Po}^+ + \text{NO}_2 \rightarrow \text{PoO}^+ + \text{NO}
\]

Therefore, A = \text{Po}^+ and B = \text{NO}_2 so that:

\[
\frac{dx}{dt} = k_2 [\text{Po}^+][\text{NO}_2]
\]

[27]

\[
t_{\text{XN2}} = \frac{[\text{Po}^+]}{(\text{d}[x]/\text{d}t)^{-1}} (k_2 [\text{NO}_2])^{-1}
\]

[28]

At T = 300 K (18, eq. [26]):

\[
k_2 = 1.410 \times 10^{14} \text{ cm}^3/\text{mole-s}
\]

[29]

Since the bond that is broken in 3 is a N-O bond, \(E_A\) must at least be greater than \((1/10)(\text{BE(O-NO)})\). Since BE(O-NO) = 3.17 eV (15), the smallest value that \(E_A\) would probably be is 0.317 eV. Therefore, from [29] \(k_2\) can be no larger than 6.819 \times 10^8 cm^3/mole-s.

\([\text{NO}_2]\) can most easily be calculated if one assumes that a negligible percentage of it reacts. One can make this assumption only if \([\text{Po}^+] << [\text{NO}_2]\). Yet one can prove this. First of all, one knows that \([\text{NO}_2] = 10\text{ppm} = 4.065 \times 10^{-10} \text{ moles/cm}^3\) and that \(C_1 = 7500 \text{ pCi/l}\). Secondly, \([\text{NO}_2]\) must be much greater than \([\text{Po}^+]\) for all feasible concentrations of \(\text{Po}^+\). The greatest \([\text{Po}^+]\) results if one assumes that it builds up and diffuses throughout the tube without decaying or reacting with \(\text{NO}_2\).
Therefore:

\[ [\text{Po}^+] = v_c - v_D \]  \[ (30) \]

\( y_c = [\text{Po}^+] \) \( \) created by Rn decay (mol/cm\(^3\))

\( y_D = [\text{Po}^+] \) \( \) decrease because of diffusion (mol/cm\(^3\))

Since 88% of Po-218 atoms are born positively charged, then:

\[ v_c = c(t_R) = 0.06 \times 10^{-3} \text{(mol/cm}^3\text{)} t_R (\text{s}) \]  \[ (31) \]

\( c = (0.88)(0.037)c_1 \) (molecules/liter-s)

\( t_R = \) smallest residence time of matter within the diffusion tube (s)

Assuming that no Po\(^+\) reacts, \( y_D \) is equal to the concentration created by Rn decay minus the actual concentration after time, \( t_R \). Then:

\[ y_D = v_c - y_c = A \left( \frac{A + \pi D}{4} \right) \left( \Delta n \right) \left( \text{cm}^3 \text{mole}^{-1} \right) \frac{y_c}{\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}} = \frac{A D}{4 t_R} \]  \[ (32) \]

\( t_R = \frac{V}{A D} = 39 \times 10^{-3} \text{(cm}^2\text{s}) / 1 \times 10^4 \text{(cm/s)} = 3.9 \times 10^{-5} \text{s} \]  \[ (33) \]

\( A = \) diffusion tube's cross sectional area = \( V/L \) (cm\(^2\))

\( D^+ = \) diffusion coefficient of Po(218)\(^+\) ions (cm\(^2\)/s)
From \([30]\) through \([33]\) one gets:

\[
[Po^+]_r = Act_r \text{e}^{(A + B) t} \quad A = 1.5 \times 10^{-22} \text{ cm}^3/\text{molecule} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \quad [30]
\]

\[
[C]_r = \text{concentration of C at the residence time (moles/cm}^3)\]

Therefore, if one now assumes a negligible loss of \(NO_2\) during reaction, from \([28]\) one gets:

\[
l_{\text{rxn}} = 6.81 \times 10^4 \text{ cm}^3/\text{molecule} \cdot 9.96 \times 10^{-11} \text{ cm}^3/\text{molecule} \cdot \text{cm} \cdot \text{sec}^{-1} = 6.6 \text{ cm} \]

In conclusion, since \(l_{\text{rxn}} > t_0\), one would expect a low \(D\) value for this reaction mechanism. Yet since \(D\) indicates effective neutralization at a \([NO_2] = 10\text{ppm}\), the mechanism is not an appropriate one.

D. Electron Scavenging Mechanism

Since \(D\) points to neutralization at this low \(NO_2\) concentration, the \(NO_2\) probably neutralizes \(Po^+\) by an electron scavenging mechanism and not by either of the first two mechanisms. \(NO_2\), though, would not be the first molecule that has neutralized \(Po^+\) ions and other positive ions by such a mechanism, since \(H_2O\) has been suggested as an electron scavenger(1). Cobine(19) first observed that positive ions have lower diffusion coefficients in dry air than in wet air. Porstendorfer and Mercer(11) found out that the diffusion coefficient of neutral
Pb-212(ThB) is .068 cm$^2$/s by collecting all charged Pb ions on a negative electrode before the resulting neutral species could be drawn through the diffusion tube. This D value did not change with different relative humidities. By removing the electrode, $D_n$, which is no more than just $D$, could then be calculated. By knowing $r$, the original percentage of Pb ions that had been absorbed on the electrode, $D_n$ could then be calculated from the following equation (11):

$$D_{ni} = rD_+ + (1-r)D_n$$

In dry air $D_+ = .024$ cm$^2$/s, but in 30-90% relative humidity $D_+ = D_n = .068$ cm$^2$/s.

Madelaine (20) was the first to find out that a higher percentage of Po-218 daughters are positively charged in dry air than in wet air. Thomas and LeClare (2) then found out that in the 20-90% relative humidity range, the diffusion coefficient of Po-218 indicates neutralization. Below 20% relative humidity D in air falls rapidly but smoothly from .085 to .053 cm$^2$/s. Kotrappa and Raghunath (21) found a D value in Ar of .0725 and .0713 cm$^2$/s for 10% and 90% relative humidity, respectively.

The mechanism whose effects all of these people have observed can be described as follows. In N$_2$ gas an alpha particle strips away two electrons from the Rn parent atom. As the Po daughter recoils, it becomes a highly ionized species. During its highly energetic movement
through the $N_2$ medium, it ionizes many $N_2$ molecules to their $+1$ states. When the daughter finally comes to rest, it immediately returns to the $+1$ state by removing electrons from more colliding $N_2$ molecules and from the electrons-rich species present in the area of the recoil path\textsuperscript{(11,16)}.

If the $N_2$ gas is dry, the electrons, that were stripped from the recoiling daughter, are picked up by $N_2^+$ ions in the vicinity. On the other hand, if $H_2O$ is present, a $H_2O$ molecule may scavenge an electron and transport it to the daughter ion. The following equation describes the mechanism\textsuperscript{(1)}:

\[ 4 \ Po^+ + e(H_2O)^- \rightarrow 4 \ H_2O \]

Although there is an electrostatic attraction between the two interacting species, neutralization by a scavenger mechanism still requires a fairly high ratio of scavengers to positive ions. Therefore, a fairly high concentration of $H_2O$ is needed in order to observe appreciable neutralization of $Po^+$ ions\textsuperscript{(1)}. For this reason if $NO_2$ were also a scavenger, it also would have to be around in fairly high concentrations before neutralization would be observed. The concentration at which it effectively neutralizes $Po$-218 is a function of its scavenging ability. $H_2O$, for one, effectively neutralizes $Po^+$ at 20% relative humidity. At $T = 300$ K, the vapor pressure of $H_2O$ is equal to 27 torr\textsuperscript{(15)}. Therefore, at RH=20% $P_{H_2O} = 7.11 \times 10^{-3}$ atm, and in turn, $[H_2O] = 7110$ ppm. On the other hand, $NO_2$ effectively neutralizes
Po ions when $[NO_2] \sim 10$ ppm $< 7110$ ppm. In short, it is an electron scavenger, it is much more effective than water vapor.
IV. Experimental

A. Setup

The experimental apparatus is outlined schematically in Figure 1. The following lower case letters correspond to points in the figure.

a) Gases: The only gases used in this experiment were \( N_2 \) (NO. Industrial Gases) and 12ppm \( NO_2 \) in \( N_2 \) (Linde). Two \( N_2 \) tanks were needed. One tank pumped \( N_2 \) through the Rn bubbler while the other \( N_2 \) tank diluted the \( NO_2 \) concentration to the desired total \( NO_2 \) concentration:

\[
\left[ NO_2 \right] = 1.2 \times 10^{-4} \left( cm^3/sec \right).
\]

\[
Q_{Rn} = Q_{N2} + Q_{NO2}.
\]

\( Q_{Rn} \) = \( N_2 \) flow rate through Rn bubbler (cm\(^3\)/s)

\( Q_{N2} \) = flow rate of \( N_2 \) dilution (cm\(^3\)/s)

\( Q_{NO2} \) = flow rate of \( N_2 \) with 12ppm \( NO_2 \) (cm\(^3\)/s)

The \( N_2 \) gas flow through the Rn bubbler was regulated with a Fischer and Porter flowmeter (model 448-225, sapphire). The correct proportions and amounts of the experimental gases were regulated by a Matheson mixer, using a
Figure 2

Experimental Setup

FM: Flowmeter
Q_n: Flowrate

Vent

Q*: Flowrate
Q_g

Vent

FM

[b] c

FM

N_2

Q_{N_2}

Q_{NO_2}

[a]

N_2

N_2

NO_2
model 600 flowmeter for the NO$_2$ in N$_2$ and one or two model 603 flowmeters for the N$_2$ diluent. Care was taken so that O$_{Rh}$ was not diluted to the point where the error in C$_1$ was on the order of C$_1$ itself.

b) Humidifier: The only purpose of this first bubbler was to humidify the N$_2$ gas flowing into the Rn bubbler. This humidity prevented the RaCl$_2$ solution from evaporating off as fast as it would have if dry N$_2$ had been bubbled through the RaCl$_2$ solution(2).

c) Rn source: The source, throughout this experiment, was 3.5 mCi of RaCl$_2$ diluted with deionized water. Any Rn gas that was generated by the decay of Ra-226 was picked up in the wet N$_2$ gas stream and was removed from the bubbler. Because the N$_2$ stream was water saturated prior to entering the Rn bubbler, the RaCl$_2$ solution was only replenished with water at one hundred hour intervals of experimentation(2). According to Thomas and LeClare(2), if air is bubbled through the RaCl$_2$ source for 24 hrs./day, it generates a very consistent C$_1$. For this system, 8 hrs. of flow through the source prior to experimentation was found to satisfy the condition for consistent C$_1$.

d) Drier: In order to remove the water, the Rn flow was forced through a cannister of anhydrous calcium sulfate(Hammond Drierite Co.). Since even traces of water do neutralize Rn daughters and do, in turn, raise the diffusion coefficient, the flow, entering the diffusion tube, had to
be completely dry.

e) Start-Stop Valve (S-S Valve): After the Rn and experimental flows had merged, the total stream could have either been diverted out a vent or been forced through the diffusion tube system.

f) Flow Regulator: This valve controlled the exact flow rate \( Q_g \) through the diffusion tube by allowing excess flow to leave the system.

g) Diffusion Tube: \( Q_g \) was then forced through a cylindrical, stainless steel diffusion tube \( (L=75 \text{ cm}, V=5919 \text{ liters}) \). At the inlet port to the tube, a glass fiber filter (Whatman, 3.7 cm) was properly cut and was placed in front of the flow in order to collect any Rn daughters that did not diffuse to the tube wall during the collection time, \( t \). Glass fiber filters were preferred over membrane and molecular sieve filters because glass fiber does not preferentially attract positive ions over neutral species while the other filter types do(2).

h) \( Q_g \) Flowmeters: In order to reduce back pressure effects to a minimum, these flowmeters were placed after the tube rather than before it. For flow rates below 30 cm\(^3\)/s, \( Q_g \) was diverted through a Fischer and Porter (model 440-118, stainless steel, precision = .1273 cm\(^3\)/s) while above 30 cm\(^3\)/s an Aalborg (034-395, sapphire, precision = .6410 cm\(^3\)/s) measured \( Q_g \). The gas flow from this point onwards was blown out the vent.
i) Detector: A Beckman gas flow (90% argon-10% methane) proportional counter was used to detect the alpha emitting Rn daughters. An Am-241 (0.9 uCi) source was used to calibrate its counting efficiency (E = 0.445).

B. Computer Program

A computer program was written in order to calculate the diffusion coefficient (DIFFCO) for specific concentrations of NO₂. A complete listing is provided in Appendix I. This program can also calculate C₁ (RAC) for each individual flow rate and can derive one C₁ value (YINT) from a least squares fit of the C₁ versus μ (MU) line. This program basically takes any low value for D and all flow rate and count information, and it continuously reform the D value in a numeric graph of C₁ versus μ. When a zero slope, weighted, least-squares fit (LSF) straight line appears numerically on the graph such that the slope (SLOPEC) is less than its standard deviation (SIGSLF), the appropriate D value and the LSF C₁ value are reported. Errors in flow rate precision and counts are propagated throughout the program, and the counting error is assumed to result only from a normal distribution around each count total.

After the program calculates a specific D value, RAC can be plotted versus MU to demonstrate the zero slope line that can be drawn through the data points. Such a graph was drawn using the 50ppb NO₂ in N₂ results (fig. 3).
Figure 1

INLET RN CONC. (PCI/L)

$U = \frac{(P_1)D_L}{Q}$
C. Procedure

Prior to running the experiment, \( \text{N}_2 \) gas was bubbled through the \( \text{RaCl}_2 \) solution for at least 8 hrs., and the detector was purged with the methane-argon gas flow for fifteen minutes. Each experiment consisted of at least three groups of five flow rates each (6.83, 14.0, 38.33, 50.0, 65.0 or 70.0 cm\(^3\)/s). After each group of flow rates the two inlet filters were replaced while the exit filter obviously was changed after each contamination. Prior to the first run, the experimental gas was turned on so that \( \dot{Q}_{\text{NO}_2} \) and \( \dot{Q}_{\text{N}_2} \) were properly adjusted for that day’s experiment. The S-S valve was then turned to the start position. The flow regulator was then adjusted until either the Fischa or the Analyti flowmeter indicated the desired value of \( \dot{Q}_p \). After turning the S-S valve to stop, the exit filter was replaced. As soon as the S-S valve was turned back on, the timer has started. At the t = 5 m mark the flow was diverted again. During this integrated buildup, a detector plate was washed with ethanol and was dried thoroughly. A piece of two-sided tape was then attached to its clean surface. After the flow was diverted, the exit filter was removed from the exit port and was lightly tapped onto the plate with the bombarded side facing upwards. After the filter was taped down, a sheet of X-ray film was taped over it in order to trap all of the recoiling nuclei and to prevent these nuclei from contaminating the detector’s window. Care was taken so that no part of the film was touching any part of the filter. At \( T_m = 1 \text{ m} \), 45 s the plate with the filter on it was pushed inside the detector. The detector’s counter was turned on at \( T_m = 2 \text{ m} \) and automatically was
turned off 10 minutes later ($T_2 = 12$ m). The background count, determined for that day, was then subtracted from the displayed count, and the resulting value was recorded.
V. Discussion

A. Problem

At the start of this investigation into the neutralization mechanism of Po\(^+\) in NO\(_2\), it was hoped that diffusion coefficients could be measured for a range of NO\(_2\) concentrations. Therefore, these D values could have been plotted versus their respective NO\(_2\) concentrations. From this plot a range of partial neutralization would have been proposed because at a certain point in this range, D would have risen smoothly with increasing NO\(_2\) concentration. It is anticipated that there would be a smooth rise because Thomas and LeClare\(^2\) found a similarly smooth rise in percent neutralization in the 0-20% relative humidity range. Yet only the 50ppb NO\(_2\) experiment worked successfully. Apparently during the period between this run and several other attempted runs, the NaCl\(_2\) solution was contaminated, since every NO\(_2\) dilution after the 50ppb run including no NO\(_2\) lead to high diffusion coefficients, indicating neutralization. Therefore, neutralization was taking place even without the presence of a neutralizing agent in the experimental gas.

During this time of trial when the high D problem was being investigated, two other serious solutions were considered and were rejected. For one, a time dependent diffusion coefficient could also lead to this puzzling value for D. This would be so if the [NO\(_2\)] that was being studied, brought about intermediate neutralization, for in
this concentration range $t_{\text{rxn}}$ is of the same order of magnitude as $t_D$. At the same time, $t_D$ is directly related to the residence time, $t_r$. Therefore, at high flow rates and at small $t_r$, $t_D < t_{\text{rxn}}$ so that very little neutralization would be detected. Yet at low flow rates and high $t_r$, $t_D$ would be too large for $D$ to detect anything but neutralization. In turn, an artificially high diffusion coefficient could result. Since $D$ still pointed toward neutralization with no NO$_2$ present, $D$'s time dependency on an intermediate [NO$_2$] could not explain the reason for the high diffusion coefficients. This time dependency, though, should definitely be investigated in a future experiment.

Another solution was also considered and was rejected too. Since Thomas and LeClare's buildup equations (2) are based on constant Rn daughter arrival at the exit filter, the Rn concentration within the tube must be the same at $t=0$ as it is at $t=5m$. In short, their equations assume that Rn gas is uniformly distributed throughout the tube at $t=0$. Prior to this realization, the $Q_g$ filter was located at the S-S valve at $t=0$ so that no daughters even reached the exit filter for a time period of at least the tube's residence time. Since $t_r$ at small $Q_g$ is much more significant than $t_r$ at large $Q_g$, a greater negative counting error would be realized at low flow than at high ones. Therefore, a falsely higher $D$ would result. This residence time problem was corrected by allowing the gas to flow through the tube at the prearranged flow rate while replacing the exit filter. The Rn gas was then trapped in the tube by turning off the S-S valve and by replacing
the exit port simultaneously. After quickly attaching the exit port, the S-S valve was turned back on, and the timer was started. This alteration in procedure did raise the count total of $Q = 6.83\, \text{cm}^3/\text{s}$ by approximately 10%. Yet since no other flow rate results were significantly affected, $D$ was only slightly lowered.

B. Conclusion

At $[\text{NO}_2] = 50\text{ppb}$ a low diffusion coefficient was observed (Appendix 2). This $D$ value indicates that no neutralization took place at this NO$_2$ concentration. According to Goldstein [22], 1.0ppm NO$_2$ in N$_2$ does effectively neutralize PO$_4^-$ ions. Therefore, it would be worthwhile to investigate the 50ppb to 1.0ppm range for the NO$_2$ concentration range in which partial neutralization occurs. The point of effective total neutralization by NO$_2$ can then be compared with H$_2$O's point of 7110 ppm, and the relative electron scavenging ability of NO$_2$ can then be deduced.
VI. References


12. This calculation assumes that the radius of a neutral Po atom is approx. 1.9Å (13), and that the radius of a N₂ molecule can be calculated from its van der Waal volume, \( b = \left(\frac{a}{3}\right)^{1/3} \). \( b(\text{N}_2) = 39.13 \text{ cm}^3/\text{mole}\) (14) so that \( r(\text{N}_2) = 2.494 \text{ Å} \). Therefore, since \( r = \left[ r(\text{Po}) + r(\text{N}_2) \right] \) and since \( m = 218 \text{ g/mole} \), D can be calculated.


15. These two sets of reactions are based on the reactions in Frey's
Yet Frey claimed, without basis, that Po was in the +2 state before reacting. His claim is false because even though Po is ionized to the +2 state or greater during its recoil, it immediately removes electrons from the colliding neutral gas molecules at the end of its recoil path (16). Therefore, Po ions are stable only in the +1 state whenever they are in a gaseous medium (11).


18. Since Po* is reacting with N\textsubscript{2}, and not with N\textsubscript{2}, the collision cross section between Po* and NO\textsubscript{2} is approximately the reaction cross section. Also since Po* is a smaller ion than Po is an atom, one can accept that r(Po*) < r(Po) = 1.9 Å (13). Therefore if one assumes that r(Po*) is one-half the Po-Po bond length, r(Po*) = 1.672 Å (15). Secondly, r(NO\textsubscript{2}) can be calculated from its van der Waal volume. b(NO\textsubscript{2}) = 44.24 cm\textsuperscript{3}/mole so that r(NO\textsubscript{2}) = 2.598 Å (15). From this data, AB = \[ \frac{r(Po^*)^2 + r(NO_2)^2}{2} \].


Appendix 1

Listing of Computer Program DIFFIT to Calculate Experimental Diffusion Coefficients
C DIFFUSION COEFFICIENT CALCULATION
C
C VARIABLE DEFINITION FOR MAIN PROGRAM
C
C QC(J) = FLOW RATE IN CC PER SEC
C SICQC(J) = EXPERIMENTAL STD. DEV. OF THE FLOW RATE
C DIFFCO(L) = ESTIMATE OF DIFFUSION COEFFICIENT IN SC PEA SEC
C K1 = 0.450/z*e**v
C K2 = PIM
C NQCS = # OF FLOW RATES
C NTRY = # OF TRIALS PER FLOW RATE
C NX(I,J) = # OF COUNTS
C SIGX(I,J) = STD. DEV. OF # OF COUNTS
C SIGAVX(J) = STD. DEV. OF THE WEIGHTED AVG. OF # OF COUNTS
C AVGX(J) = WEIGHTED AVG. OF # OF COUNTS
C MU(J,L) = K2*DIFFCO(L)/QC(G)
C FRACF(J,L) = F OF F
C RAC(J,L) = RADON CONC. IN PCI PER LITER
C SIGRAC(J,L) = STD. DEV. OF RADON CONC.
C SLOPEC(L) = SLOPE OF RADON CONC. VS. MU
C SIGSLO(L) = STD. DEV. OF SLOPEC
C YINT(L) = Y INT. OF RADON CONC. VS. MU
C SIGINT(L) = STD. DEV. OF YINT
C SIGF(J) = STD. DEV. OF F OF F
C SIGMU(J) = STD. DEV. OF MU
C SIGD(J) = STD. DEV. OF DIFFUSION COEF.
C AVSIGD = AVG. OF SIGD
C MUVE(D) = SLOPE OF MU VS. F OF F
C MODE = NO. WHICH DETERMINES THE LSF WEIGHTING FACTOR
C 1: WEIGHT=1.
C 0: WEIGHT=1./SIGRAC**2
C FROM AN ESTIMATE OF THE DIFFUSION COEFFICIENT WE WILL APPROACH A ZERO
C SLOPE LINE FOR THE GRAPH OF RADON CONC. VS. MU. AT THIS POINT,
C THE EXACT VALUE OF THE DIFFUSION COEFFICIENT WILL BE KNOWN.
C
PROGRAM DIFFIT (INPUT, OUTPUT, TAPE5=INPUT, TAPE6=OUTPUT)

REAL QC(10),DIFFCO(30),K1,K2,SIGX(6,10),SIGAVX(10),
ZAVGX(10),MU(10,30),SICQC(10),
ZFRACF(10,30),RAC(10,30),SICRAC(10,30),SLOPEC(30),SIGSLO(30),
ZYINT(30),SIGINT(30),SIGF(10),SIGMU(10),SIGD(10),AVSIGD,MUVE(D)
DIMENSION NX(6,10)
READ(5,*)NQCS,NTRY,K1,K2,DIFFCO(1),MODE
35 FORMAT(213,2F4.0,F5.0,F6.0)
READ(5,*)SICQC(J),J=1,NQCS)
DO 100 J=1,NQCS
   READ(5,*)QC(J),(NX(1,J),I=1,NTRY)
55 FORMAT(F6.0,616)
   DO 80 I=1,NTRY
      NX=NX(I,J)
      SIGX(I,J)=SQRT(AXX)
     80 CONTINUE
   CALL XF1TUOC,SICX,NTRY,AVCX(j),SlCAVX(J),J)
100 CONTINUE
C PREVIOUSLY A LOW EST. OF THE DIFF. COEF. WAS READ. NOW THE DIFF.

C COEF. WILL BE INCREASED IN INCREMENTS, UNTIL IT IS GREATER THAN ITS
C EXACT VALUE. THEN THE VARIABLE L WILL BE INCREMENTED ALONG WITH
C SMALLER DECREASES IN THE DIFF. COEF.

L=1
120 DO 170 J=1,NQCS
MU(J,L)=K2*DIFFCO(L)/QG(J)
SIGMU(J)=SIGQ(J)/QG(J)**2
CALL GRAPH(MU(J,L),FRACF(J,L),MUVSF(J),DIFFCO(L))
SIGF(J)=SIGMU(J)/MUVSF(J)
RAC(J,L)=AVGX(J)/FRACF(J,L)
SIGRAC(J,L)=AVGX(J)/FRACF(J,L)**2*
Z+(SIGF(J)/FRACF(J,L))**2)
2 CONTINUE
170 CALL LINFIT(MU,RAC,SIGRAC,NQCS,YINT(L),SIGINT(L),
SLOPEC(L),SIGSLO(L),L,MODE)
IF(SLOPEC(L),1.T.0.0.AND.L.NE. 1 )GO TO 340
IF(SLOPEC(L),GE.0.)GO TO 260
DIFFCO(L)=DIFFCO(L)+.01
GO TO 120
260 DIFFCO(L+1)-DIFFCO(L)-.0005
L=L+1
1F(L.NE.30)GO TO 120
PRINT 300,(SLOPEC(L),SIGSLO(L),L=25,29)
300 FORMAT("THE SLOPE IS NOT APPROACHING ZERO. THE LAST 5 VALUES OF
ZSLOPEC AND SIGSLO ARE"/1X,3(E11.4,">" OR ""),E11.4,2X)/1X,
Z2(E11.4,">" OR ""),E11.4,2X))
PRINT 301,DIFFCO(30)
301 FORMAT("THE LAST VALUE OF THE DIFFUSION COEFF. WAS",2X,E11.4,
Z"SC PER SEC")
STOP
340 IF(ABS(SLOPEC(L)),GT.SLOPEC(L-1))L=L-1
AVSIGD=0.
DO 400 J=1,NQCS
SIGF(J)=AVGX(J)/YINT(L)*SQR(SIGAVX(J)**2/AVGX(J)**2+
ZSIGINT(L)**2/YINT(L)**2)
SIGM(J)=MUVSF(J)*SIGF(J)
SIGD(J)=MU(J,L)=QG(J)/K2*SQR(SIGM(J)**2/MU(J,L)**2+ZSIGQ(J)**2/QG(J)**2)
AVSIGD=AVSIGD+SIGD(J)
400 CONTINUE
AVSIGD=AVSIGD/NQCS
PRINT 430
430 FORMAT("1",4X,"VALUE",3X,">" OR "" STD. DEV.")
PRINT 431,DIFFCO(L),AVSIGD
431 FORMAT("THE DIFFUSION COEFFICIENT IS",17X,E11.4,">" OR ""E11.4,
Z"SC PER SEC")
PRINT*,"L= "L,
PRINT 432,SLOPEC(L),SIGSLO(L)
432 FORMAT(" THE LSF SLOPE OF RALON CONC. VS. MU 'S",8X,E11.4,">" OR ""E11.4,
ZE11.4)
PRINT 433,YINT(L),SIGINT(L)

433 FORMAT(" THE LSF RADON CONCENTRATION IS",15X,E11.4," +/-",E11.4,
2"PICOCURIES PER LITER")
PRINT 434
434 FORMAT(" OUTFLOW RATE (CC/S) ",20X,"MU",20X,"RA CONC. (PCI/L)")
PRINT 435,(QG(J),MU(J,L),RAC(J,L),SIGRAC(J,L),J=1,NQGS)

STOP
END

C END OF MAIN PROGRAM
C
C SUBROUTINE X-FIT
C THIS SUBROUTINE CALCULATES WEIGHTED AVERAGE AND THEIR CORRESPONDING
C STD. DEVIATIONS.

SUBROUTINE XFIT(X, SIGX, NPTS, XMEAN, SIGMAM, J)
INTEGER X(6,10)
REAL SIGX(6,10),SUM,SUMX
SUM=0.
SUMX=0.
DO 70 1=1,NPTS
   WEIGHT=1./SIGX(1,J)
   SUM=SUM+WEIGHT
   SUMX=SUMX+WEIGHT*X(I,J)
70 CONTINUE
XMEAN=SUMX/SUM
SIGMAM=SQRT(1./SUM)
RETURN
END

C SUBROUTINE GRAPH
C THIS SUBROUTINE WILL GIVE US VALUES OF F OF F AND MUVS FROM
C CALCULATED VALUES OF MU.

SUBROUTINE GRAPH(MU,FRACF,MUVSF,DIFFCO)
C OUTSIDE VARIABLES
REAL MU,FRACF,MUVSF
C LOCAL VARIABLES:
REAL AMU(40),AFRACF(40)
DATA (AMU(K),K=1,34)/.005,.008,.01,.02,.03,.04,.05,.06,.07,.08,
2.09,.11,.14,.16,.18,.2,.25,.3,.35,.4,.45,.5,.6,.7,.8,.9,1,1.5,
22.,25.,3,.4,.5./
DATA (AFRACF(K),K=1,34)/.877,.849,.834,.778,.737,.705,.678,.654,
2.633,.614,.596,.58,.551,.525,.502,.481,.462,.42,.384,.349,.324,
2.302,.282,.248,.22,.197,.178,.162,.11,.083,.067,.056,.042,.033/
K=1
60 IF(AMU(K).GE.MU.AND.K.NE.1)GO TO 90
IF(AMU(K).GE.MU)GO TO 70
   K=K+1
   IF(K.EQ.35)GO TO 70
GO TO 60
70 PRINT*,"YOU MESSED UP. THE MU VALUE IS NO LONGER WITHIN THE",
2" RANGE OF AMU."
PRINT*, "THE LAST VALUE OF DIFFCO WAS ", DIFFCO

STOP

90  FRAFC = AFRACF(K-1) * (AFRACF(K) - AFRACF(K-1)) * (MU - AMU(K-1)) / (AMU(K) - ZAMU(K-1))
   MUVF = (AMU(K) - AMU(K-1)) / (AFRACF(K) - AFRACF(K-1))
   RETURN

END

C
C SUBROUTINE LINFIT
C THIS SUBROUTINE PERFORMS A LEAST SQUARES FIT ON A SET OF DATA PTS.
C THE SLOPE, THE Y-INTERCEPT, AND BOTH OF THEIR CORRESPONDING STD. DEVS.
C RESULT FROM THIS WEIGHTED FIT.

SUBROUTINE LINFIT(X, Y, SIGMA, NPTS, A, SIGMAA, B, SIGMAB, L, MODE)
REAL X(10,30), Y(10,30), SIGMA(10,30)
SUM = 0.
SUMX = 0.
SUMY = 0.
SUMX2 = 0.
SUMXY = 0.
SUMY2 = 0.
DO 90 I = 1, NPTS
   X1 = X(I, L)
   Y1 = Y(I, L)
   IF(MODE) 70, 70, 80
   70   WEIGHT = 1./SIGMA(I, L)**2
   GO TO 85
   80   WEIGHT = 1.
   85   SUM = SUM + WEIGHT
   SUMX = SUMX + WEIGHT * X1
   SUMY = SUMY + WEIGHT * Y1
   SUMX2 = SUMX2 + WEIGHT * X1 * X1
   SUMXY = SUMXY + WEIGHT * X1 * Y1
   SUMY2 = SUMY2 + WEIGHT * Y1 * Y1
   CONTINUE
   DELTA = SUM * SUMX2 - SUMX * SUMX
   A = (SUMX2 * SUMY - SUMX * SUMXY) / DELTA
   B = (SUMXY * SUM - SUMX * SUMY) / DELTA
   IF(MODE) 100, 100, 110
   100   VAR = 1.
   GO TO 120
   120   SIGMAA = SQRT(VAR * SUMX2 / DELTA)
   SIGMAB = SQRT(VAR * SUM / DELTA)
   RETURN

END
Appendix 2

Results of 50ppb NO₂ in N₂ experiment
The diffusion coefficient is TOF. LSF slope of radon conc. vs. 1 is the LSF radon concentration is rate (cc/s).

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<th>Flow Rate (cc/s)</th>
<th>Value (per std. dev.)</th>
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<td>70.00</td>
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<th>Radon conc. (pCi/l)</th>
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