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RADIOLYTIC EVOLUTION OF GASES
FROM Z-9 SOILS

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INTRODUCTION

The 216-Z-9 Trench was used from 1955 to 1962 as a liquid waste disposal site for the Plutonium Finishing Plant located in the 200 West Area at Hanford, Washington. As a result, plutonium accumulated in the top two feet of soil at the bottom of the trench. The plutonium bearing soils are presently being removed for storage in a retrievable package. The soil is mined remotely, packaged, and buried so that it may be retrieved within 20 years.

The soil removed from the Z-9 Trench contains plutonium, water, and organics. The water and organics radiolyze to form hydrogen, oxygen and other gases. The evolved gas can accumulate in a storage drum, pressurizing the drum and possibly forming an explosive mixture. The possible explosion hazards which result from the trapped evolved gases provide the incentive for this study.

The objective of the study is to experimentally determine gas evolution rates from Z-9 soil samples as a function of the plutonium, moisture, and organic content of the soil.

SUMMARY

The total gas evolution rate was correlated with the plutonium and combined moisture and organic soil content (see Figure 4). The maximum measured gas evolution rate was 1.3×10^{-6} gram-mole/hour - gram of plutonium. The major components of the evolved gas were determined to be 49.5 mole percent, (M%) nitrogen, 23.3 M% hydrogen, 14.1 M% oxygen and 13.1 M% carbon dioxide. This composition was determined from gas evolved by water-rich soil. Soils which are rich in organics may evolve gas with less oxygen.

The data established the magnitude of the hydrogen evolution problem. Evolution of both oxygen and hydrogen means that the gas mixture will remain within the explosive range, once the lower explosion limit is exceeded.

EXPERIMENTAL

Soil Sampling

A list of the soil samples and experimentally determined properties ^{is} are shown in Table I. ✓

TABLE I
PROPERTIES OF Z-9 SOIL SAMPLES

Sample	Sample Source (Soil Canister Number)	Sample Weight (grams)	Plutonium Content (grams)	Organic Content (Wt. %)	Moisture Content (Wt %)	Date of Sampling
A	Mix of Z9SC-08-76-0003 Z9SC-08-76-0004	444.0	7.4*	16.2	30.0**	8/76
B	Mix of Z9SC-08-76-0005 Z9SC-08-76-0013	662.0	5.0*	8.9	30.0**	8/76
C	Mix of Z9SC-08-76-0001 Z9SC-08-76-0008	610.5	4.5*	11.1	12.9	8/76
D	Z9C-08-76-0003	615.2	4.3 $\pm$ 1.1	1.5	16.0	11/23/76
E	Z9C-08-76-0004	538.4	4.0 $\pm$ 1.0	19.3	6.2	11/23/76
F	Z9C-08-76-0008	400.8	3.9 $\pm$ 0.9	9.7	18.7	11/23/76
G	Z9C-08-76-0014	695.1	1.8 $\pm$ 0.9	3.4	7.3	11/23/76
H	Z9C-08-76-0017	586.4	2.4 $\pm$ 1.0	7.9	13.7	11/23/76

*Error not available

**Water added

The initial experiments were performed on soil samples A, B, and C. The samples consist of a mixture of soil from two different canisters. Two samples were combined in order to increase the sample size, thereby decreasing the void volume of the experimental apparatus and increasing the total gas evolution rate. The soil samples originated as process samples taken during the mining operation and were obtained by taking 250 to 300 milliliters (ml) of soil from the top of a canister. The history of samples A, B, and C for the three months which elapsed between sampling and use in the experiments is unknown.

Water was added to soil samples A and B to increase the moisture content to 30 weight percent (Wt %). This soil moisture content is higher than any soil encountered during the actual mining operation. The water was added in an attempt to establish the maximum radiolytic gas generation rate.

Soil samples D, E, F, G, and H in Table I were obtained from canisters chosen to provide a range of soil compositions. Each 500 ml sample was made up of ten 50 ml soil samples taken from different regions in the canister.

The plutonium content of each soil sample listed in Table I was determined by non-destructive assay on a Canberra segmented gamma-scanner.

After analysis for plutonium content, a ten gram sample was taken from each of the five 500 ml soil samples to determine the organic and moisture content of the soil. The small sample was obtained by stirring the 500 ml of soil in a flat, rectangular pan and filling a small vial with scoops of soil from six different areas of the pan. The ten gram sample was not returned to the 500 ml sample after heating, adding a small amount of error to the plutonium content measurement.

The soil moisture and organic contents are determined by the same methods used to analyze the Z-9 mining operation process samples. The moisture content is determined by heating the ten gram sample at 110°C for two hours. The resulting weight loss is called moisture even though it may include volatile organics contained by the soil. The organic content is determined by the weight loss which results in heating the soil from 110°C to 600°C for two hours. The results of the soil plutonium, organic, and moisture analysis are summarized in Table I.

Equipment

Flasks filled with soil and capped with an open-end manometer were used to measure the gas evolution rate of Z-9 soils. Two different types of manometer arrangements were constructed for the experiments.

The apparatus shown in Figure 1 was provided for determining gas evolution rates and allowed sampling of the gas accumulated over the soil. The apparatus shown in Figure 2, called the sealed apparatus, minimized the possible points of gas leakage and was used to measure the total gas evolution rate of a soil sample. Water with a drop of mineral oil on each end was used as the moving fluid in the manometers. The oil reduced the water evaporation rate.

The experiments were conducted in a glovebox. The absolute pressure inside the glovebox was determined using a brass-case mercury manometer. Other equipment used inside the glovebox include constant temperature water baths for each sample flask and thermometers placed in various locations.

Procedures

The volume of each flask and manometer arrangement was determined prior to placing the apparatus in the glovebox. The sample flask volume was determined by weighing the flask, before and after filling with water. The manometer assembly volume was determined by directly measuring the volume of water required to fill a particular region. A summary of the void volumes of the separate systems is shown in Appendix II, Table III (page 30).

After the volumes were recorded, the empty apparatus was tested for leaks by pressurizing the flask to approximately ten millimeters of mercury, gage, for 24 hours. The apparatus was then placed in the glovebox and the sample flask filled with the soil to be tested. The sample flask was then placed in a constant temperature water bath and the pressure equalized inside and outside the apparatus. The initial manometer readings, ambient pressure and temperature were recorded.

FIGURE 1.
GAS SAMPLING APPARATUS

FIGURE 2.
SEALED APPARATUS

The gas evolution rate from each soil sample was determined by measuring the pressure and volume changes of gas in the apparatus over a known time interval. In order to determine the amount of gas in the system, the following data was recorded: absolute pressure inside the glovebox, air temperature inside the glovebox, water bath temperature for each apparatus and the fluid level in the two legs of the manometer. Controlled amounts of gas were removed when the internal pressure reached the limit of the manometer apparatus. All the gas removed from the system was accounted for and used to determine gas evolution rates.

A sketch of the sample bulb, prepared for sampling, is shown in Figure 3. The sample bulb was evacuated before being introduced into the glovebox. After positioning the sample bulb on the apparatus, the region between the bulb and the sample flask was evacuated. Gas which accumulated above the soil was allowed to enter the evacuated volumes. Stopcocks were closed, separating the sample bulb from the gas evolving system. The sample bulb was then removed from the glovebox and monitored for contamination. The gas sample was analyzed by mass spectroscopy.

The simpler apparatus in Figure 2 was designed to minimize the potential for leaks, a major source of experimental error. Therefore, opening the system at the clamped ball-and-socket joint to equalize gas pressures was considered undesirable. Instead, when the pressure difference reaches the limit of the manometer in the sealed apparatus, gas was drawn off by a syringe and tubing arrangement. A length of thin, flexible tubing was attached to a syringe. Then, with the syringe closed, the tubing was pushed through the manometer liquid and into the gas space. The desired volume of gas was drawn into the syringe and the tubing removed.

RESULTS

Total Gas Evolution Rates

Figure 4 represents a correlation of the gas evolution rate to the combined organic and moisture content of the soil. A correlation coefficient (R^2) of 0.971 indicates that the fitted curve is a good representation of the experimental data. The correlation gives an estimate of the total gas evolution rate from a Z-9 soil sample, given the plutonium, moisture and organic content of the soil. The rate increased with the organic and water content of the soil. The organic and moisture content are combined into one parameter because both organic and water molecules radiolyze when bombarded by alpha radiation.

The gas evolution rate for each soil sample was determined by plotting the total gas in the experimental apparatus against time and fitting a curve through the data points. The data and fitted curves for each soil sample are shown in Figures 5 through 12 of Appendix I.

FIGURE 3.
GAS SAMPLE BULB

FIGURE 4.
CORRELATION OF THE GAS EVOLUTION RATE FROM Z-9 SOILS TO THE COMBINED ORGANIC
AND MOISTURE COMPOSITION

Soil samples A, B, and C have lower gas evolution rates than the other samples. Since the history of samples A, B, and C is not known, these samples are not included in the correlation with the other samples. A possible explanation for the lower rates is that all or a large part of samples A, B, and C could have been heated to determine organic and moisture contents, then returned to the same sample bottle, making the actual organic and moisture composition much less than the reported value. Inaccuracies in the plutonium assay for samples A, B, and C would also account for observed evolution rate differences. Also, water added to samples A and B in the laboratory may not accurately represent soil moisture from the trench.

Soil samples D through H are natural soils (no water added) with known histories. These soil samples all displayed an initial time period during which no gas was generated or, as in sample H, gas was absorbed. After this time interval, gas was generated at a constant rate. The pause in gas evolution is not explained at this time.

Evolved Gas Composition

The evolution rate of each gas component is determined by plotting the accumulated amount of each gas component against time. The evolution rate of each component is compared to the total gas evolution rate which yields the mole percent composition of the evolved gas. The resulting evolved gas composition is summarized in Table II. A sample calculation of evolved gas composition as determined from the gas sample analysis is shown in Appendix II. The evolved gas is mostly made up of nitrogen and nitrogen oxides. These gases may be due to the radiolysis of cadmium nitrate and nitric acid solutions which were added to the trench soils. Hydrogen, oxygen, and carbon dioxide may represent the decomposition of water and organic compounds within the soil. The composition reported in Table II was obtained for gas evolved from water rich soil. Soil which is high in organic content may evolve gases of a significantly different composition.

TABLE II
EVOLVED GAS COMPOSITION

<u>Component</u>	<u>Mole Percent</u>
Nitrogen (N ₂)	49.5
Oxygen (O ₂)	14.1
Hydrogen (H ₂)	23.3
Carbon Dioxide (CO ₂)	13.1

The repeatability of a mass spectrograph analysis was verified by splitting a gas sample. One portion of the gas sample was analyzed on the mass spectrograph, the other portion by gas chromatography. The composition determined by each analysis is shown below:

<u>Component</u>	<u>Mass Spectrograph Analysis (mole %)</u>	<u>Gas Chromatograph Analysis (mole %)</u>
Nitrogen	75.9	75.7
Oxygen	20.4	22.1
Carbon Dioxide	2.77	1.3
Hydrogen	0.07	---
Nitrous Oxide	---	<0.1
Argon	0.93	0.9*

*Argon composition assumed when normalizing volumetric ratios from the chromatograph data.

The comparison shows that the two analysis techniques give similar compositions for the same gas.

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NOMENCLATURE

- α = Thermal expansion factor for correcting barometric readings (mm Hg/°C)
- n = Gram-moles of gas in a region (g-moles), n_1 is the amount of gas in region 1, $n_{3,4}$ is the combined amount of gas in regions 3 and 4, etc.
- P = Absolute pressure, millimeters of mercury at zero centigrade (mm Hg @ 0°C), P_1 is the pressure in region 1, $P_{3,4}$ is the pressure in regions 3 and 4, etc.
- R = Ideal gas constant, $62359 \frac{\text{mm Hg @ 0°C} - \text{cc}}{\text{g-mole} - ^\circ\text{K}}$
- T = Temperature of the gas, degrees Kelvin (°K)
- V = Gas volume, cubic centimeters (cc), V_1 is the volume of region 1, $V_{3,4}$ is the combined volume of regions 3 and 4, etc.
- x_{O_2} = mole fraction of oxygen, dimensionless

APPENDIX I
DATA

FIGURE 5.
GAS EVOLUTION FROM SOIL SAMPLE A

FIGURE 6.
GAS EVOLUTION FROM SOIL SAMPLE B

FIGURE 7.
GAS EVOLUTION FROM SOIL SAMPLE C

FIGURE 8.
GAS EVOLUTION FROM SOIL SAMPLE D

FIGURE 9.
GAS EVOLUTION FROM SOIL SAMPLE E

FIGURE 10.
GAS EVOLUTION FROM SOIL SAMPLE F

FIGURE 11.
GAS EVOLUTION FROM SOIL SAMPLE G

FIGURE 12.
GAS EVOLUTION FROM SOIL SAMPLE H

FIGURE 13.
TOTAL GAS, NITROGEN AND OXYGEN EVOLUTION FROM SOIL SAMPLE A.

FIGURE 14.

HYDROGEN, CARBON DIOXIDE AND ARGON EVOLUTION FROM SOIL SAMPLE A

APPENDIX II

GAS EVOLUTION RATE CALCULATIONS

The increased amount of gas is calculated using the ideal gas law

$$PV = nRT \quad (1)$$

where the symbols are defined in the nomenclature. The changes in gas pressure, volume, and temperature within the sample flask were recorded after a time interval.

DETERMINATION OF GAS VOLUME

The experimental apparatus is divided into regions (see Figures 15 and 16) and the volume of each region is determined (see Table III). Soil is then added to the sample flask and the gas evolution rate measured. The volume of interest in each apparatus will be the volume of region 1 and 2 minus the particle volume of the soil (this accounts for the volume of gas within the voids of the soil).

Sample Calculation of the Void Volume

For Soil Sample A,

Sample weight = 444.0 grams (g)
 Plutonium content = 7.4 g
 Moisture content = 8.4 weight percent (Wt %)
 Organic content = 16.2 Wt %

The organic material is assumed similar in weight to a soil particle, weight of dry solid in A = $444.0g (1 - 0.084)$
 $= 406.6 g$

This is a poor assumption. Later calculations, assuming an organic density of 1 g/cc, estimate the resulting apparatus volume error to be less than 5 percent.

The density of basalt and feldspar ranges from 2.5 to 2.7 grams per cubic centimeter (g/cc), therefore, assuming a particle density of 2.7 g/cc (Reference 1), the particle volume = $\frac{406.6g}{2.7 g/cc} = 150.6 cc$

Water was added to Sample A until the moisture content reaches 30 Wt %, therefore, the weight of water in the sample was $0.30(\frac{406.6g}{0.7}) = 174.3 g$

and the volume of water in the sample is 174.3 cc.

FIGURE 15.

VOLUME REGIONS OF SAMPLING APPARATUS, VOLUMES LISTED
IN TABLE III

FIGURE 16.

VOLUME REGIONS OF SEALED APPARATUS, VOLUMES LISTED
IN TABLE III

TABLE III
VOLUME OF REGIONS IN THE
GAS EVOLUTION APPARATUS

Soil Sample Apparatus	VOLUME REGIONS (Figures 15 and 16)			
	V_I^* (cc)	V_{II}^{**} (cc)	V_{III} (cc)	V_{IV} (cc)
A	587.0 ± 1.0	17.0 ± 0.4	14.9 ± 0.4	10.0
B	587.0 ± 1.0	17.0 ± 0.4	14.9 ± 0.4	10.0
C	478.1 ± 0.2	14.0 ± 0.2	----	----
D	480.4 ± 0.2	15.4 ± 0.2	----	----
E	593.6 ± 0.4	12.8 ± 0.4	15.0 ± 0.6	10.0
F	479.2 ± 0.2	15.6 ± 0.2	----	----
G	482.3 ± 0.2	16.0 ± 0.2	----	----
H	486.5 ± 0.2	15.6 ± 0.2	----	----

Manometer tube volume = 0.0962 cc /linear cm

* Volume of empty flask.

**Volume when manometer is zeroed.

From Table 3, for Sample A,

$$V_1 = 587.0 \text{ cc and } V_2 = 17.0 \text{ cc}$$

Therefore, the gas volume within the apparatus at the start of the experiment is

$$587.0 + 17.0 - 150.6 - 174.3 = 279.1 \text{ cc}$$

The volume of region 2 increases and decreases with the level of the manometer fluid. The volume change is determined by the diameter of the manometer tubing. Assuming a 1 cm length of tubing,

$$\begin{aligned} \text{Inside diameter of tubing} &= 0.35 \text{ cm} \\ \text{Change in volume} &= \frac{(1 \text{ cm}) (0.35 \text{ cm})^2 \pi}{4} = 0.0962 \text{ cc/cm of fluid level change} \end{aligned}$$

Gas Constant, R (reference 1)

$$R = 62359 \frac{\text{mm Hg @ } 0^\circ\text{C} - \text{cc}}{\text{g-mole} - ^\circ\text{K}}$$

Determination of the Gas Pressure in Regions 1 and 2

After each time interval, the following data was recorded:

Barometer Reading In Glove Box (mm Hg @ Air Temp)	Air Temperature (°C)	Water Bath Temperature (°C)	Manometer Readings (inches of water)		
			Sample Side	Hood Side	Diff
756.8	23.7	23.0	-3.25	+3.40	+6.65

The values are representative numbers from sample A, which will be used in sample calculations.

The barometric reading inside the glovebox is corrected for thermal expansion as follows:

$$\text{Barometric Reading} = 756.8 \text{ mm Hg @ } 23.7^\circ\text{C}$$

From Table 1, Page 365 of reference 2,

$$\begin{aligned} \alpha &= 0.123 \text{ mm Hg}/^\circ\text{C} \text{ (for brass case)} \\ \text{and the correction} &= \alpha(t_1 - t_2) \\ &= 0.123 (23.7 - 0) \\ &= 2.9 \text{ mm Hg} \\ \text{The hood pressure} &= 756.8 - 2.9 \\ &= 753.9 \text{ mm Hg @ } 0^\circ\text{C} \end{aligned}$$

The gage pressure of gas in the apparatus,

$$\begin{aligned} &(6.65 \text{ in. of water}) (1.868 \text{ mm Hg @ } 0^\circ\text{C/in. of water}) \\ &= 12.4 \text{ mm Hg @ } 0^\circ\text{C} \end{aligned}$$

The absolute pressure of gas in the apparatus,

$$P_{1,2} = 753.9 + 12.4 = 766.3 \text{ mm Hg @ } 0^{\circ}\text{C}$$

The change in total gas volume due to expansion into the manometer leg is

$$\begin{aligned} & (3.25 \text{ inch}) (2.54 \text{ cm/inch}) (0.0962 \text{ cc/cm of tube}) \\ & = 0.8 \text{ cc} \end{aligned}$$

Determination of Evolved Gas Composition

Representative Raw Data (from Run 8, Sample A)

$$\begin{aligned} P_{1,2} \text{ before sampling} &= 766.3 \text{ mm Hg @ } 0^{\circ}\text{C} \\ V_{1,2} \text{ before sampling} &= 279.9 \text{ cc} \\ P_{1,2,3,4} \text{ after sampling} &= 734.4 \text{ mm Hg @ } 0^{\circ}\text{C} \\ V_{1,2} \text{ after sampling} &= 276.5 \text{ cc} \\ V_{3,4} &= 24.9 \text{ cc} \end{aligned}$$

Composition of Air:

<u>Component</u>	<u>Mole %</u>
CO ₂	0.07
Ar	0.94
O ₂	21.0
N ₂	78.0

Analysis of Gas Sampled: (By Mass Spectroscopy)

<u>Component</u>	<u>Mole %</u>
CO ₂	2.62
Ar	0.91
O ₂	16.3
N ₂	74.8
CO	<0.10
He	<0.01
H ₂	5.37
CH ₄	<0.10
N ₂ O	0.52
NO _x	0.01
C ₂ H _x	0.2
C _x H _y	0.1

Oxygen lost from system during previous samplings:

$$= 3.90 \times 10^{-4} \text{ g-moles}$$

Air dilution of the gas sample:

$$(n_{1,2} + n_{3,4}) \text{ before opening stopcocks} = (n_{1,2,3,4}) \text{ after sampling}$$

Therefore, the air pressure in regions 3 and 4 before sampling is

$$P_{3,4} = \frac{(734.4)(276.5 + 24.9) - (766.3)(279.9)}{24.9}$$

$$= 275.5 \text{ mm Hg @ } 0^\circ\text{C}$$

$$\text{and } n_{3,4} = \frac{(275.5)(24.9)}{(62359)(296.7)} = 3.71 \times 10^{-4} \text{ g-moles}$$

which is the amount of air already in the sampling bulb (region 3 and 4)

Oxygen composition of gas over soil moisture:

Total gas leaving 1 and 2, and entering 3 and 4 during sampling =

$$0.01162 - 0.01100 = 6.2 \times 10^{-4} \text{ g-moles}$$

Total gas in 3 and 4 after sampling,

$$6.2 \times 10^{-4} + 3.71 \times 10^{-4} = 9.91 \times 10^{-4} \text{ g-moles}$$

The oxygen composition of the gas over the soil is determined by an oxygen balance around regions 3 and 4

$$x_{O_2} (6.2 \times 10^{-4}) + (0.21)(3.71 \times 10^{-4}) = (0.163)(9.91 \times 10^{-4})$$

$$x_{O_2} = 0.135$$

of the gas over the soil is 13.5 percent oxygen.

The total oxygen in the system shown on Figure 13 after 27.5 days, including oxygen lost during sampling, is:

$$3.90 \times 10^{-4} + (0.135)(0.01162) = 1.96 \times 10^{-3} \text{ g-mole}$$

Oxygen lost from system in sampling is

$$(0.135)(6.2 \times 10^{-4}) = 8.37 \times 10^{-5} \text{ g-moles}$$

For the next run, the oxygen lost from the system is incremented to

$$3.90 \times 10^{-4} + 8.37 \times 10^{-5} = 4.737 \times 10^{-4} \text{ g-mole}$$

A calculation similar to that shown for oxygen can be done for each component.

Evolved Gas Components:

Slopes from curves on Figures 13 and 14 are determined and mole fractions calculated by dividing each of these slopes by the slope of the total gas curve.

<u>Component</u>	<u>Rate (g-mole/day)</u>	<u>Mole Fraction</u>
N ₂	7.43×10^{-5}	60.9
O ₂	2.13×10^{-5}	17.4
CO ₂	1.97×10^{-5}	16.1
H ₂	3.49×10^{-5}	28.6
Ar	0	0
Total Gas	1.22×10^{-4}	--

The mole fractions are the normalized to yield the evolved gas composition shown in Table II.

APPENDIX III

EXPERIMENTAL ERROR

EVOLUTION RATE ERROR

The error equation for the ideal gas law is as follows (reference 3)

$$n = \frac{PV}{RT}$$

$$\Delta n = \left| \frac{\partial n}{\partial P} \right| \Delta P + \left| \frac{\partial n}{\partial V} \right| \Delta V + \left| \frac{\partial n}{\partial T} \right| \Delta T$$

Where $\frac{\partial n}{\partial P} = \frac{V}{RT}$ $\frac{\partial n}{\partial V} = \frac{P}{RT}$ $\frac{\partial n}{\partial T} = -\frac{PV}{RT^2}$

For the absolute pressure,

$$\Delta P = \Delta P_{\text{Hood}} + \Delta P_{\text{Gas}}$$

$$\Delta P_{\text{Hood}} \approx \pm 0.5 \text{ mm Hg}$$

$$\Delta P_{\text{Gas}} = \pm 0.25 \text{ inch of water} \\ \pm 0.5 \text{ mm Hg}$$

Therefore,

$$\Delta P \approx \pm 1.0 \text{ mm Hg}$$

For the volume measure,

$$\Delta V = \Delta V_{\text{measured volume}} + \Delta V_{\text{Particle Volume}} + \Delta V_{\text{Soil Moisture}} + \Delta V_{\text{manometer Volume}}$$

$$\Delta V_{\text{Manometer}} \approx (0.0962 \text{ cc/cm})(2.54 \text{ cm/in})(\pm 0.25 \text{ in}) = \pm 0.1 \text{ cc}$$

$$\Delta V_{\text{Soil Moisture}} \approx \pm 1 \text{ cc}$$

$$\Delta V_{\text{Measured Volume}} \approx \pm 5 \text{ cc}$$

$$V_{\text{Particle Volume}} = \frac{\text{Sample Weight (Wt)}}{\text{Particle Density } (\gamma)}$$

Therefore,

$$\Delta V_{\text{Particle Volume}} = \frac{Wt}{\gamma} + \frac{Wt}{\gamma^2}$$

$$Wt \pm 400 \pm 0.1 \text{ g}$$

$$= 2.7 + 0.5 \text{ g/cc}$$

$$\Delta V_{\text{Particle Volume}} = \frac{0.1}{2.7} + \frac{400}{(2.7)^2} (0.5) = 27.5 \text{ cc}$$

and $\Delta V = 5 + 27.5 + 1 + 0.1 = + 33.6 \text{ cc}$

For the temperature,

$$\Delta T \pm 1^\circ\text{K}$$

For Sample A,

$$P = 749.1 \text{ mm Hg} \quad V = 279.1 \text{ cc}$$

$$T = 298^\circ\text{K} \quad R = 62359 \frac{\text{mm Hg} \cdot \text{cc}}{\text{g-mole} \cdot ^\circ\text{K}}$$

$$\Delta n = \text{Pressure Err} + \text{Volume Err} + \text{Temperature Err}$$

$$\begin{aligned} \Delta n &= \frac{279.1}{(62359) 298} (1.0) + \frac{749.1}{(62359) 298} (33.6) + \frac{(749.1)(279.1)}{(62359)(298)^2} (1.0) \\ &= 1.5 \times 10^{-5} + 1.4 \times 10^{-3} + 3.8 \times 10^{-5} \\ &= \pm 0.00145 \text{ g-mole} \end{aligned}$$

The error in the particle volume estimate dominates the total evolved gas error. This volume is a constant, therefore, for the data shown on Figures 5-12, large errors are associated with each point, but the error in the difference from point to point is small.

Gas Composition Errors

The largest error in the gas composition was due to the sampling procedure. Vacuum lines in the glovebox provided vacuums ranging from 60 to 500 mm of mercury for sampling gas, therefore, a dilution factor was required in order to determine the composition of the gas over the soil. The many ground glass joints and stopcocks of the gas sampling apparatus and the pressurized system provided many possible leak points for evolved gases to escape. After a sample was obtained, the sample bulb was transported to the Hanford Engineering Development Laboratory for analysis by mass spectroscopy. The time lapse between sampling and analysis usually amounted to four hours, allowing further dilution of the sample if the sample bulb contains any leaks.