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April 1996

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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Executive Summary

This report summarizes progress made in evaluating mechanisms by which flammable gases are generated in Hanford double-shell tank wastes, based on the results of laboratory tests using actual waste from Tank 241-SY-103. Work described in this report was conducted at Pacific Northwest National Laboratory (PNNL)[a] for the Flammable Gas Safety Project, the purpose of which is to develop information needed to support Westinghouse Hanford Company (WHC) in its efforts to ensure the safe interim storage of wastes at the Hanford Site. This work is related to gas generation studies being performed at Georgia Institute of Technology (GIT), under subcontract to PNNL, using simulated wastes, and to studies being performed at WHC using actual wastes.

The objective of this work is to establish the identity and stoichiometry of degradation products formed in actual tank wastes by thermal and radiolytic processes as a function of temperature. The focus of the gas generation tests on Tank 241-SY-103 samples is first the effect of temperature on gas generation (volume and composition). Secondly, gas generation from irradiation of Tank 241-SY-103 samples at the corresponding temperatures as the thermal-only treatments will be measured in the presence of an external radiation source (using a ^{137}Cs capsule). The organic content will be measured on a representative sample prior to gas generation experiments and again at the termination of heating and irradiation. The gas generation will be related to the extent of organic species consumption during heating.

Described in this report are 1) experimental methods used for producing and measuring gases generated at various temperatures from highly radioactive actual tank waste, and 2) results of gas generation from Tank 241-SY-103 waste taken from its convective layer. The accurate measurement of gas generation rates from actual waste from highly radioactive waste tanks is needed to assess the potential for producing and storing flammable gases within the waste tanks. This report addresses the gas generation capacity of the waste from the convective layer of Tank 241-SY-103, a waste tank listed on the Flammable Gas Watch List due to its potential for flammable gas accumulation above the flammability limit.

The gas reaction system developed in earlier work using simulated waste was modified to accommodate the needs of operations within the hot cell facility used for the actual waste samples in this study. Verification tests were designed to challenge the system's ability to measure the quantity of gas at various temperatures and pressures similar to those required in gas generation tests. It was demonstrated that the quantity of gas was accurately modeled using the ideal gas law and that the temperatures, volumes, and pressure of each system were accurately assessed. In all, 12 independent reaction systems (10 in use, two spares) were fabricated and tested prior to use with actual waste. In all cases, the ability of each system to measure the quantity of gas within the system was reproducible and excellent.

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The waste samples from Tank 241-SY-103 used in this study are measured under two conditions: first, with externally applied heat and second, with externally applied heat and radiation (^{137}Cs capsule). In the thermal experiments discussed in this report, the self radiolysis of the sample was not negligible and must be considered to understand the total gas generation. The self-dose rate of the actual waste was calculated based on the known inventory of radionuclides and chemical composition of the waste as well as the geometry and construction of the reaction vessel. The calculated self dose rate is 119 rad/hr averaged over the entire sample, assuming a 14.7 mL sample in a flat-bottomed stainless (304) steel vessel. More than 99% of the absorbed radiation dose comes from the decay of ^{137}Cs (beta and gamma). The second phase of the work, in which the waste is introduced to an external gamma field, is currently being investigated and will be described in a subsequent report.

A main objective of this work is to establish the identity and stoichiometry of degradation products formed in actual tank wastes by thermal and radiolytic processes as a function of temperature. The focus of the gas generation tests on Tank 241-SY-103 samples is first on the effect of temperature on the composition and rate of gas generation. Generation rates of nitrogen, nitrous oxide, and hydrogen increased with increased temperature, though at different rates. As such, composition of the product gas mixture varied with temperature. The fraction of nitrous oxide increased with increased temperature in the range 60 to 120°C, the fraction of nitrogen decreased, and the fraction of hydrogen was essentially unchanged. The consequences of changes in relative concentrations of gases will be seen in differences in activation energies for the production of these gases.

Arrhenius treatment of the rate data revealed activation parameters for the gas generation from Tank 241-SY-103. The activation energy for total gas formation is 94 ± 6 kJ/mole (95% confidence level). Based on the rate of formation of each component gas in the systems, activation energies were calculated. The activation energies (E_a) for formation of these components are 80 ± 8 kJ/mole (95% confidence interval) for N_2, 90 ± 9 kJ/mole for H_2, and 116 ± 9 kJ/mole for N_2O.

Measuring gas generation from the waste from Tank 241-SY-103 is a continuing project. The second phase of this work is the study of the gas generation capacity of Tank 241-SY-103 waste in the presence of an external gamma source. This work is being performed during the last half of FY 1996. In addition to the gas generation from the thermal and radiolytic treatment of the tank waste, the organic components of the waste are being analyzed. The waste is being analyzed for specific organic components before and after heating and radiolysis to help identify the organic species responsible for gas generation. By following the specific organic species present and their concentration changes as a function of heating and irradiation, together with the results of measurements of the gases formed during the heating and irradiation treatments, an understanding of the organics responsible for gas generation is possible. The gamma-assisted gas generation and organic analysis of the waste will be reported in a subsequent document.

Contents

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1.0 Introduction

This report describes the status of research to measure gas generation from actual waste taken from the convective layer of Tank 241-SY-103. Two topics are presented: 1) experimental methods used for producing and measuring gases generated at various temperatures from actual highly radioactive tank waste, and 2) results of gas generation from Tank 241-SY-103 waste taken from the convective layer of that tank. Work described in this report is being conducted at Pacific Northwest National Laboratory (PNNL) for the Hanford Waste Tank Safety Flammable Gas Program, whose purpose is to develop information needed to support the interim safe storage of nuclear and chemical wastes at the Hanford Site. This work, requested by Westinghouse Hanford Company (WHC), started in FY 1995 and continues into FY 1996.

The gas generation tests on Tank 241-SY-103 samples are focused first on the effect of temperature on gas generation (volume and composition), and second on measuring gas generation from irradiation of Tank 241-SY-103 samples in the presence of an external radiation source (^{137}Cs capsule). The organic content will be measured on a representative sample prior to gas generation experiments and again at the termination of heating and irradiation. The gas generation will be related to the extent of organic species consumption during heating.

The tank waste samples and radiation source are contained within the hot cell. Gas measurement equipment is contained in an adjacent hood, attached to the reaction vessels by small-diameter stainless steel tubing. Current plans are to complete measurements on Tank 241-SY-103 convective layer samples and begin tests on samples from Tank 241-AW-101. The tests will establish gas generation rates from actual waste samples as a function of temperature, with and without sample irradiation. From these results, apparent activation energies can be calculated that will allow gas generation rates at other temperatures to be estimated.

To assess the effects of temperature on gas generation of 241-SY-103 convective layer samples, gas generation experiments were performed in duplicate at five temperatures (60, 75, 90, 105, and 120°C) for a total of ten reactions (five temperatures x two replicates). Organic analyses were performed on the waste samples before and after gas generation experiments to establish the contribution of organics toward gas generation. Organic analyses are being performed by the Actual Waste Organic Analysis task and include determination of TOC (total organic carbon) as well as specific organic species within the waste.

Section 2 of this report describes the gas generation test sample and the experimental conditions and equipment used for the gas generation tests. Section 3 presents the results and discussion from the gas generation experiments. A summary of results is included in Section 4; Section 5 contains the references cited.

2.0 Experimental Methods for Gas Measurements

Gas generation tests on actual radioactive tank waste was conducted at PNNL's High Level Radiochemistry Facility in the 325 Building (325A HLRF). The material examined was provided by the WHC Characterization program, which obtained the core samples from Tank 241-SY-103. Gas generation measurements are being made using reaction vessels and a gas manifold system similar to that used in earlier studies with simulated waste (Bryan and Pederson 1995).

A description of the test material from Waste Tank 241-SY-103 is included in Section 2.1. Section 2.2 contains a description of the gas generation test equipment that was developed for earlier studies on non-radioactive waste simulants and has been modified for use in a radiological hot cell. The self-dose rate from the radionuclide inventory in Tank 241-SY-103 samples was calculated to assess the amount of radiation chemistry from internal sources. These calculations are included in Section 2.3. Section 2.4 contains results for testing and verification of the gas reaction system. The procedure for starting the reaction and sampling gases at the termination of experiments is given in the appendix.

2.1 Tank 241-SY-103 Test Material

The material examined for this report was provided by the WHC Characterization program, which obtained core samples from Tank 241-SY-103. The liquid core samples from the convective layer were combined to give one large representative sample (Wilkins 1995). From this combined sample of the convective layer of Tank 241-SY-103, 300 grams of original and undiluted material was taken for shipment to PNNL for gas generation testing. This sample was delivered to the High Level Radiochemistry Facility in four separate shipments due to the size limitations of the shipping cask. The four sub-samples were recombined in the 325 hot cell facility and stirred to ensure homogeneity.

The liquid appeared colorless (through the hot cell leaded glass window) with a small amount of solids present. The glass container containing the convective layer sample became cloudy from solids deposited on the walls. A photograph of the recombined Tank 214-SY-103 convective layer sample used for these gas generation experiments is shown in Figure 1.

2.2 Experimental Conditions and Equipment

Gas generation measurements were made using reaction vessels and a gas manifold system similar to that used in earlier studies with simulated waste (Bryan and Pederson 1994, 1995). The reaction vessels are connected to the gas manifold using small-diameter stainless steel connecting tubing. Each reaction vessel has its own pressure transducer connected to the gas manifold line of each vessel. The entire surface of the reaction system exposed to the waste sample is stainless steel, except for a gold-plated copper gasket sealing the flange at the

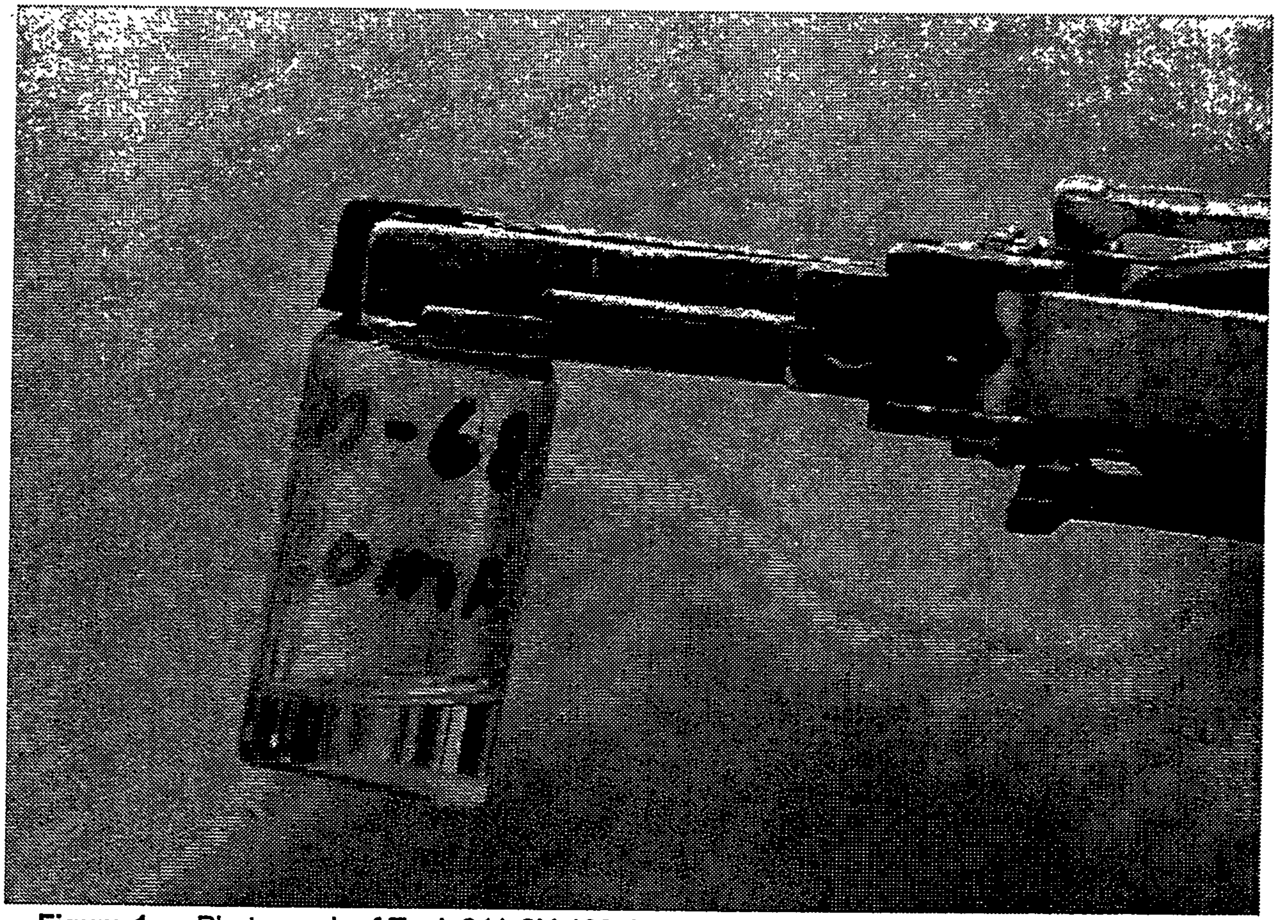

Figure 1. Photograph of Tank 241-SY-103 Convective Layer Sample Used in Gas Generation Testing (photograph was taken through the hot cell window)

top of the reaction vessel. Figure 2 shows the placement of the thermocouples within and on the reaction vessel. A schematic diagram of the gas manifold system with the placement of the reaction vessels relative to the gas manifold system is shown in Figure 3. Pressures and temperatures were recorded with a CR10 datalogger (Campbell Scientific, Inc., Logan, Utah). The datalogger was programmed using Campbell Scientific's Edlog program for DOS.

The reaction vessels were constructed of 304 stainless steel. The reaction space of the vessel is a cylinder approximately 5/8-inch (1.59 cm) in diameter by 8 -1/4 inches(20.96 cm) high. Each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body of the reaction vessel to allow for temperature control and over-temperature protection. Two thermocouples were inserted through the lid of the vessel. The thermocouple centered in the lower half of the vessel monitors the temperature of the liquid phase; the thermocouple centered in the upper half monitors the gas phase temperature within the reaction vessel. The reaction vessels are placed in a hot cell and are connected by a thin (0.0058-cm inside diameter) tube to a gas manifold outside the hot cell. A stainless steel filter (60-micrometer pore size, Nupro brand) protects the tubing and manifold from contamination. A thermocouple is also attached to the filter.

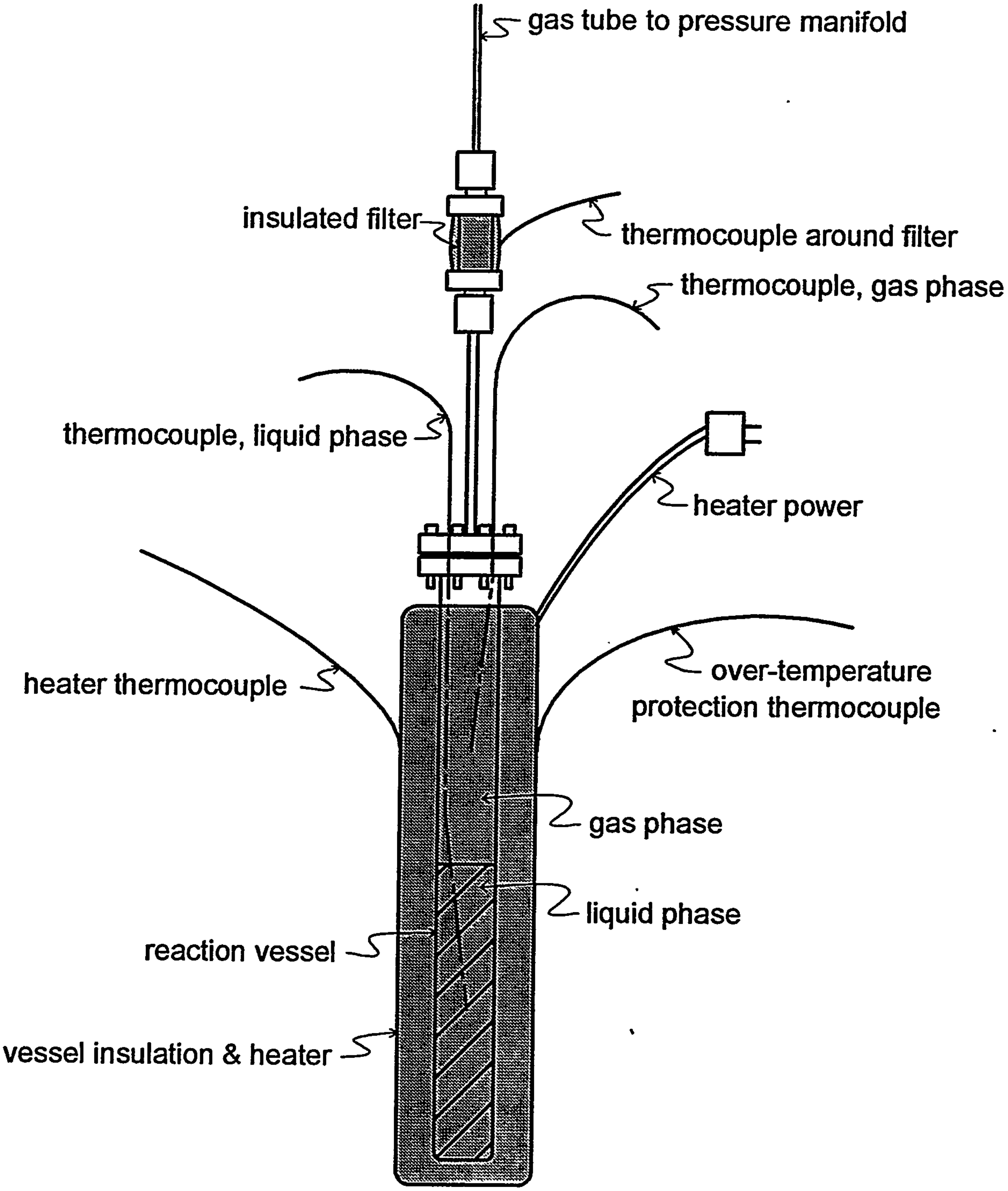

Figure 2. Diagram of Gas Generation Reaction Vessel

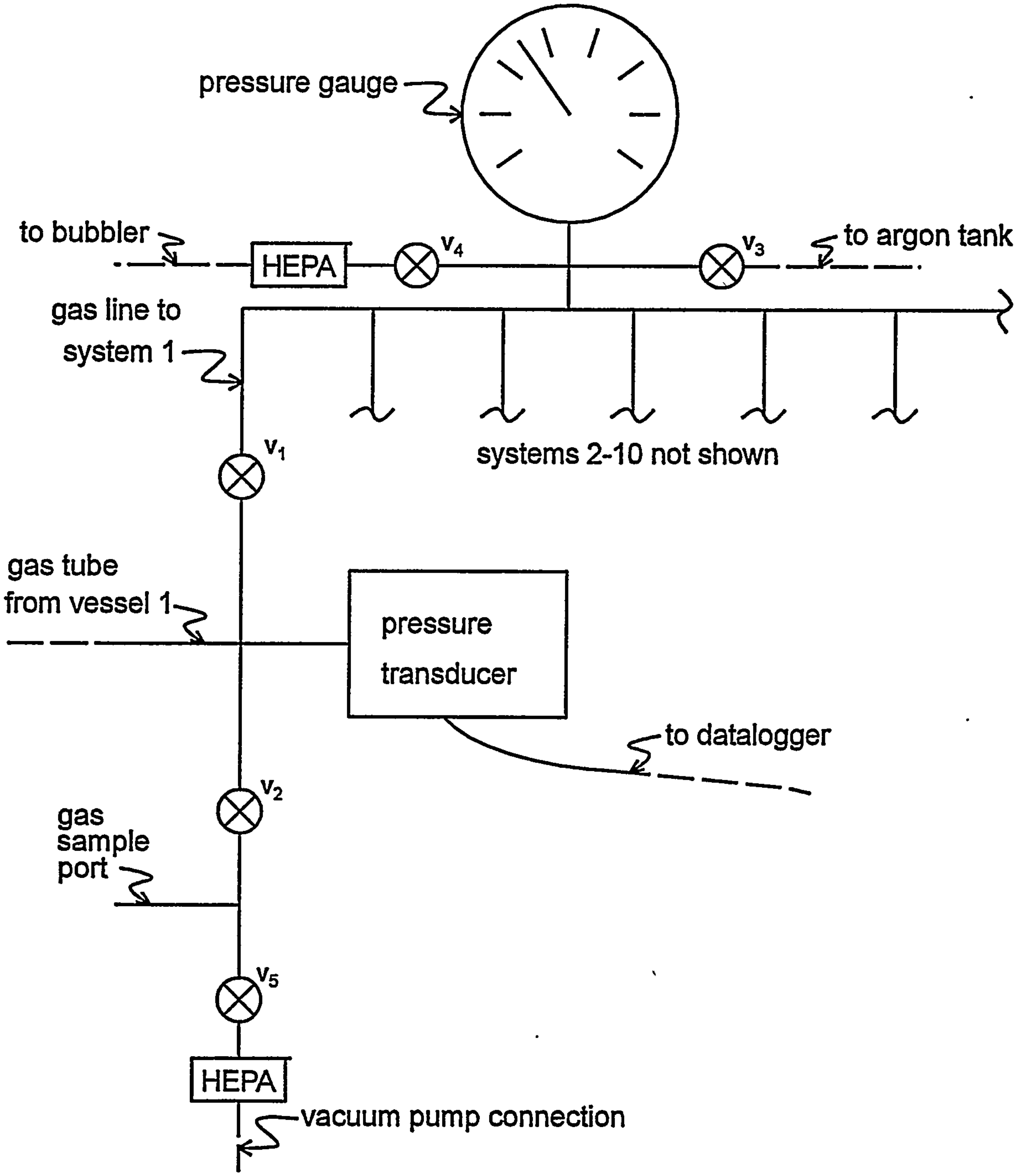

Figure 3. Schematic Diagram of Gas Generation Reaction Manifold System

Total moles of gases in the system were calculated from the pressure, temperature, and volume of each thermal region of the gas phase:

$$\text{moles}_{\text{total}} = \text{moles}_{\text{vessel}} + \text{moles}_{\text{filter}} + \text{moles}_{\text{manifold and tubing}}.$$

The manifold volume and filter volume were determined from pressure/volume relationships using a calibrated gas manifold system. The manifold volume on the vessel side of valve **V1**, which consists of the pressure sensor, valves, and miscellaneous fittings, was 3.99 mL. The filter volume was 1.34 mL; the tubing volume was 1.715 mL (by calculation); the cap stem (the tube from vessel to filter) has a volume of 0.20 mL; half of that was added to the filter volume, giving 1.44 mL, and half was added to the vessel volumes. The volume of each vessel was determined gravimetrically by filling it with water. These volumes are recorded in Table 1, along with the mass of convective layer added to each vessel and the gas phase volume in the vessel after the sample was added. The density of the convective layer was 1.48 ± 0.01 g/mL (95% confidence interval), which agrees well with the value of 1.47 g/mL previously reported (Wilkins 1995).

Each system has a separate pressure transducer, which was sealed on the back side. Because the back was sealed, measured pressures were independent of changes in atmospheric pressure. However, they did depend on the temperature of the gas in the back side, since an increase in temperature caused an increase in pressure. To compensate for this, the temperature of the manifold, T_{manifold}, was recorded with each pressure measurement. The actual pressure is gauge pressure + atmospheric pressure. Since the gas trapped in the back side of the gauge is nearly atmospheric, the actual pressure is taken to be $P_{\text{actual}} = P_{\text{measured}} + (P_{\text{atmospheric}} \times T_{\text{manifold}}/T_{\text{ref}})$, where T_{ref} is the reference temperature (absolute) of the manifold at the start of the reaction, and T_{manifold} is the temperature (absolute) of the manifold at the time of the pressure measurement.

At the start of a reaction, each system was purged by three or four cycles of pressurizing with argon at 40 psi (276 kPa) and venting to the atmosphere. The systems were heated to about 60°C for an hour to drive dissolved gases out of solution. They were then purged again and left at atmospheric pressure, about 745 mm Hg (99.3 kPa). Valve **V1** was then left closed for the remainder of the reaction. The vessels were then heated and the set points adjusted to

Table 1. Sample Mass, Vessel Volume, and Vessel Gas Phase Volume for each System

	SYSTEM									
	1	2	3	4	5	6	7	8	9	10
Temperature, °C	60	60	75	75	90	90	105	105	120	120
Sample mass, g	21.97	22.39	22.42	22.47	22.45	22.43	22.41	22.439	22.39	22.42
Vessel volumes										
Total, mL	33.17	33.17	33.27	33.37	33.37	32.90	33.17	29.65	33.30	33.45
Gas phase, mL	18.25	17.97	18.03	18.15	18.14	17.69	17.91	14.42	18.05	18.22

keep the liquid phase within 1°C of the desired temperature. Thermal equilibrium was achieved usually within 30 minutes, which also signaled the start of each gas generation experiment. The relatively short thermal equilibrium time was not deemed a significant error compared with the total time for each gas experiment (usually >100 hr). The liquid phase temperatures were 60, 75, 90, 105 and 120°C ± 1°C. The temperature of the gas phase was approximately 10 - 25°C lower than liquid phase. Procedures for starting reactions and sampling gases are included as an appendix to this report.

At the end of each reaction, the vessels were allowed to cool overnight, then a sample of the gas was taken. The metal gas collection bottles had a volume of approximately 75 mL and were equipped with a valve. The bottle, after being evacuated overnight at high vacuum, was attached to the gas sample port. Air was removed from the region between valves **V2** and **V5** with a vacuum pump. After the collection bottle was removed, the bottle and sample port were surveyed for radioactive contamination. No contamination was ever found.

We assumed that gases in the reaction system were well-mixed, a reasonable assumption. Samples are withdrawn through the capillary line into an evacuated bulb. The volume of the capillary line is small, less than 2 mL, whereas the gas phase of the reaction vessel volume is ≈15 mL in all cases, and the collection bulb volume is ≈75 mL. Because gases will move by viscous flow through the capillary tube in this pressure regime, we did not anticipate that significant errors would be introduced by using this procedure. The excellent agreement between calculations of total gas generated from compositional data and from pressure rise data (see Figure 10 and associated text in Section 3.2, below) demonstrates that there is no error introduced by this sampling method.

Analyses of the composition of the gas phase of each reaction vessel after each reaction were performed according to analytical procedure PNNL-MA-599 ALO-284, Rev 1, by the Mass Spectroscopy Facility staff operated by PNNL and located in the 325 Building. The amount of a specific gas formed during heating is given by the mole percent of that gas present multiplied by the total moles of gas present in a system.

After collecting the gas generation data, 1 mL of the material in each vessel and 5 mL of unheated material were sent to PNNL's Analytical Chemistry Laboratory in the 325 Building for organic analyses. The organic components of the convective layer will be analyzed under the Actual Waste Organic Analysis task according to procedures outlined in Campbell et al. 1994. The organic analysis is still under way; these data will be reported in a subsequent report that will also include the gamma enhanced gas generation data.

2.3 Self-Dose Rate from Radionuclide Inventory in Tank 241-SY-103 Samples

Gamma dose rates were calculated by PNNL's Health Protection Department using the program MCNP (Monte Carlo N-Particle Transport Code System) (Briesmeister 1993). This program uses the Monte Carlo method, in which a radiation particle or photon is emitted in random directions from random locations in the sample. The probabilities of the radiation being absorbed by the sample and reflected from the container wall back into the sample are known (Kocher 1981). Input to the program includes the composition of the vessel walls, the composition of the bulk of the sample, and the radionuclides present (the last two are given in Wilkins [1995]). The output is the amount of radiation absorbed by the sample averaged over the entire sample.

The self-radiolysis dose of a 14.7 mL sample in a flat-bottomed stainless (304) steel vessel was calculated. The energy deposition/dose results for the convective layer of the tank using a density of 1.47 g/mL and a composition of 48.4 wt% water, 9.73 wt% NO_2, 12.18 wt% NO_3, 14.4 wt% Na, and 2.82 wt% Al were

^{137}Cs beta decay:	1.82E+6 (MeV/sec)/gram or 105 rad/hr
^{137}Cs gamma decay:	2.46E+5 (MeV/sec)/gram or 14.2 rad/hr

The total dose is 119 rad/hr averaged over the entire sample. More than 99% of the absorbed radiation dose comes from the decay of ^{137}Cs (beta and gamma). The dose rate contribution from ^{90}Sr was insignificant and could be ignored.

Using the same assumptions as above, the calculated dose rate from the convective layer of Tank 241-SY-103, within the tank, is 339 rad/hr from ^{137}Cs gamma and 105 rad/hr from ^{137}Cs beta for a total dose rate of 444 rad/hr. Therefore, the waste samples used in the gas generation tests reported here will receive approximately 27% of the total dose of an equivalent sample within the actual waste tank.

2.4 Verification of Gas Reaction System

To ensure that the moles of gas could be measured correctly when the reaction vessel temperature was changed, we performed an experiment in which a known quantity of gas was measured at various reaction vessel temperatures. The reaction vessel temperature was changed from a starting temperature of 60°C to 90° and finally to 120°C, then decreased through 90°C to 60°C as the final temperature. This temperature range encompasses the experimental range that will be encountered during gas generation tests. The pressure increased as the temperature increased, following the Ideal Gas Law. The moles of gas within the closed reaction system remains constant throughout the experiment.

The reaction vessel temperature of a reaction vessel attached to the gas manifold line in the same configuration used for gas generation experiments is shown in Figure 4. The temperature of the reaction vessel was initially regulated at 60°C for approximately 20 hours. At that time, the temperature of the reaction vessel was quickly increased to 90°C and allowed to stay at this temperature for approximately five hours. The temperature was again increased to 120°C and allowed to stay at that temperature for several days. The temperature was then lowered to 90°C for a short time (about one hour) followed by a return to the original temperature of 60°C. The pressure of the gas in the system increased as the temperature increased and decreased as the temperature decreased, as expected for a fixed volume system; it is shown in Figure 5. Comparing Figures 4 and 5, we see that the pressure tracks the temperature very well.

The moles of gas were calculated using pressure-volume-temperature relationships in which each portion of the reaction system the volume and temperature were measured and the total pressure of the system was known. For example, in system 1, the total moles present, 0.00155, ranged from a maximum of 0.00157 to a minimum of 0.00152 over the entire temperature range. The relative standard deviation (RSD) of total moles during this experiment was only 0.56%. For the experiment shown in Figures 4 and 5, the total moles of gas within the reaction system as a function of time was calculated and is shown in Figure 6. For the entire experiment's duration, in which the temperature was changed from 60°C to 120°C and then back to 60°C, the calculated moles of gas were constant.

This experiment was repeated for all of the reaction systems used in actual waste testing. Each reaction vessel was attached to a separate gas manifold line and increased from 60 to 120°C and back to 60°C, as described for reaction vessel 1. The pressures, temperatures, and moles of gas were monitored for each reaction system. Table 2 contains the results for reaction systems 1 through 10. In each case, the error in moles calculated was less than 2% RSD, ranging from 0.19 to 1.99%. In all cases, the ability of each system to measure its quantity of gas was reproducible and excellent.

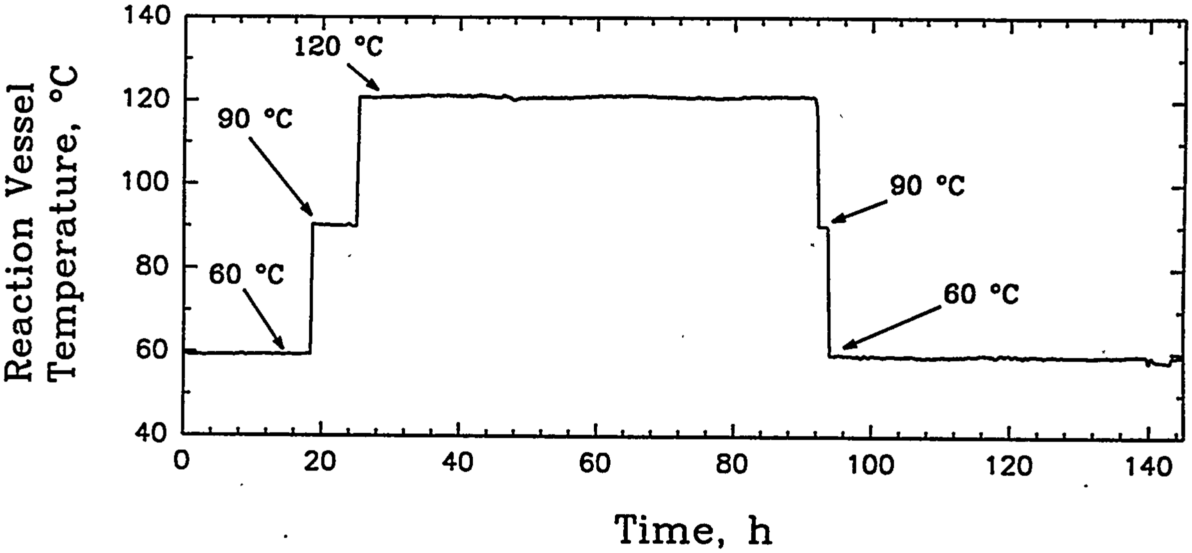

Figure 4. Reaction Vessel Temperature During Initial Testing (temperature of the reaction vessel was changed from 60 to 90 to 120°C and back to 60°C during this experiment)

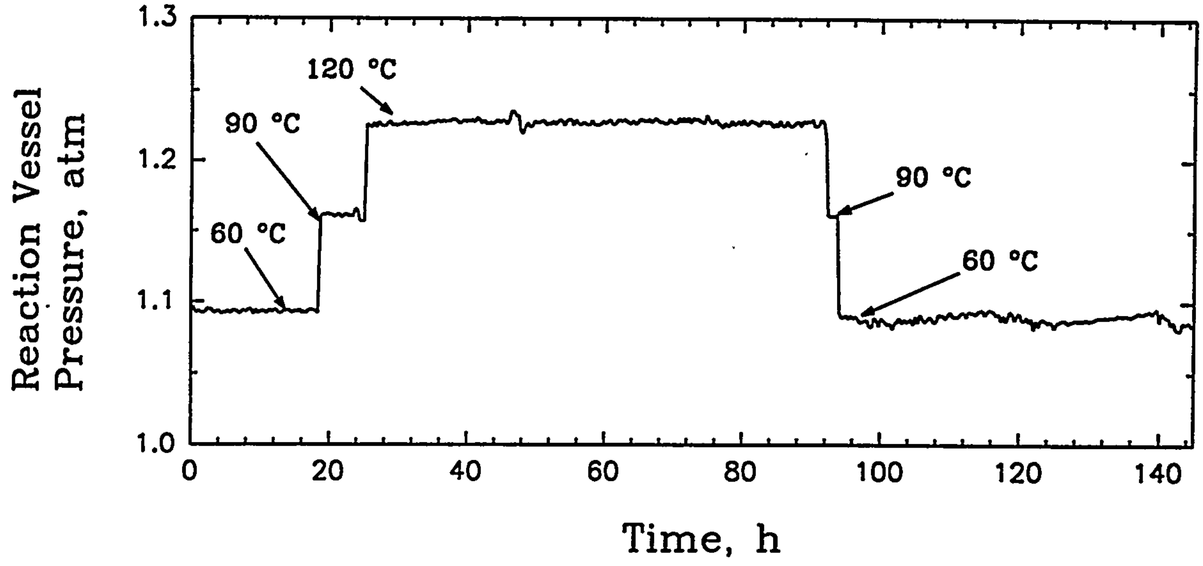

Figure 5. Reaction Vessel Pressure During Initial Testing (the temperature of the reaction vessel was changed from 60 to 90 to 120°C and back to 60°C during this experiment)

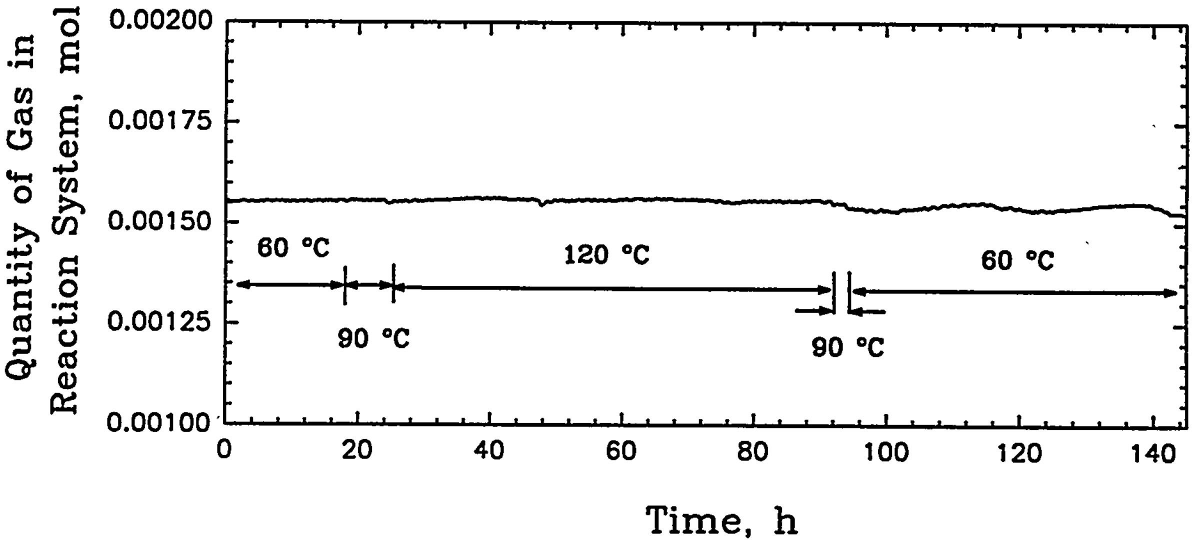

Figure 6. Total Moles of Gas in Reaction System During Initial Testing (the temperature of the reaction vessel was changed from 60 to 90 to 120°C and back to 60°C during this experiment)

Table 2. Measured Moles of Gas Contained in Gas Manifold System During Heating and Cooling System Check

	SYSTEM									
	1	2	3	4	5	6	7	8	9	10
Moles (average)	1.55E-3	1.69E-3	1.67E-3	1.95E-3	5.21E-3	2.35E-3	1.67E-3	1.68E-3	1.56E-3	1.69E-3
Maximum moles	1.57E-3	1.70E-3	1.69E-3	1.97E-3	6.42E-3	2.40E-3	1.69E-3	1.70E-3	1.64E-3	1.71E-3
Minimum moles	1.52E-3	1.68E-3	1.65E-3	1.94E-3	5.13E-3	2.30E-3	1.65E-3	1.67E-3	1.54E-3	1.67E-3
Standard Deviation	8.72E-6	3.08E-6	9.34E-6	1.02E-5	1.04E-4	3.39E-5	1.32E-5	9.26E-6	2.22E-5	8.43E-6
RSD	0.56%	0.18%	0.56%	0.52%	1.99%	1.44%	0.79%	0.55%	1.43%	0.50%

3.0 Gas Generation from Tank 241-SY-103 Waste Samples

The focus of the gas generation tests on Tank 241-SY-103 samples is first on the effect of temperature on gas generation. Section 3.1 addresses on the composition of gases generated from the convective layer of Tank 241-SY-103 waste samples. The rate of gas generation from Tank 241-SY-103 as a function of temperature is a second primary goal of this work. The rate of gas generated from Tank 241-SY-103 waste as a function of temperature is discussed in Section 3.2. Along with total gas generated, this section also summarizes the rate of generation of component gases from the convective layer as a function of temperature. These rate data are used to calculate the activation energy of gas formation from Tank 241-SY-103 waste; these calculations are included in Section 3.3.

3.1 Composition and Generation Rates of Gases from Tank 241-SY-103 Convective Layer

The amount of gas produced versus heating time is shown in Figure 7 for duplicate systems at each of five temperatures (ten "Runs"). Generally three to four gas samples (Sample "a" through "d") were taken from each reaction system over a period of approximately 400 to 800 h. The entire gas generation reaction (Run) is comprised of the three or four consecutive samples. The amount of gas produced is normalized for the amount of sample present, giving units of moles of gas produced per kg of convective layer, moles/kg. The data included in Figure 7 are for all gas measurements for each of the five temperatures for which gases were collected. The gas generation rates for each gas sample are given in Table 3 and the total moles of gas within each reaction system at the termination of each reaction is given in Table 4.

The rate of gas generation is distinctly different at each temperature studied, as can readily be seen in Figure 7. For example, the gas generation for the 60° and 75°C systems are observably different, and the amount of gas formed in the 60°C system, though small, is distinguishable from zero.

The gas generation data in Figure 7 are distinctly curved, especially the data at 105°, and 120°C. This curvature was unexpected, since production of gas from simulated tank material has usually been described as linear under similar reaction conditions (Bryan and Pederson 1994). A plausible explanation is that the waste material contains many different components, of which the most reactive are depleted within the time scale of the experiment. As their concentration diminishes, the gas generation rate decreases. An attempt to fit the plot to a mathematical expression (such as a first-order reaction or a sum of two first-order reactions) failed in that duplicate systems gave widely different results. It is standard practice to record data for at least two half-lives of a reaction before developing a kinetic model to fit these data. The present experiment lasted less than a single half-life, even for the 120°C systems; therefore, attempting to fit this data to a mathematical expression is not justified.

The rate of gas formation for each sample is given in Table 3. The units used for rates in this report are moles of gas formed per kg convective layer per day of heating (mole/kg/day). The rates in Table 3 were determined from the difference between moles present at the start

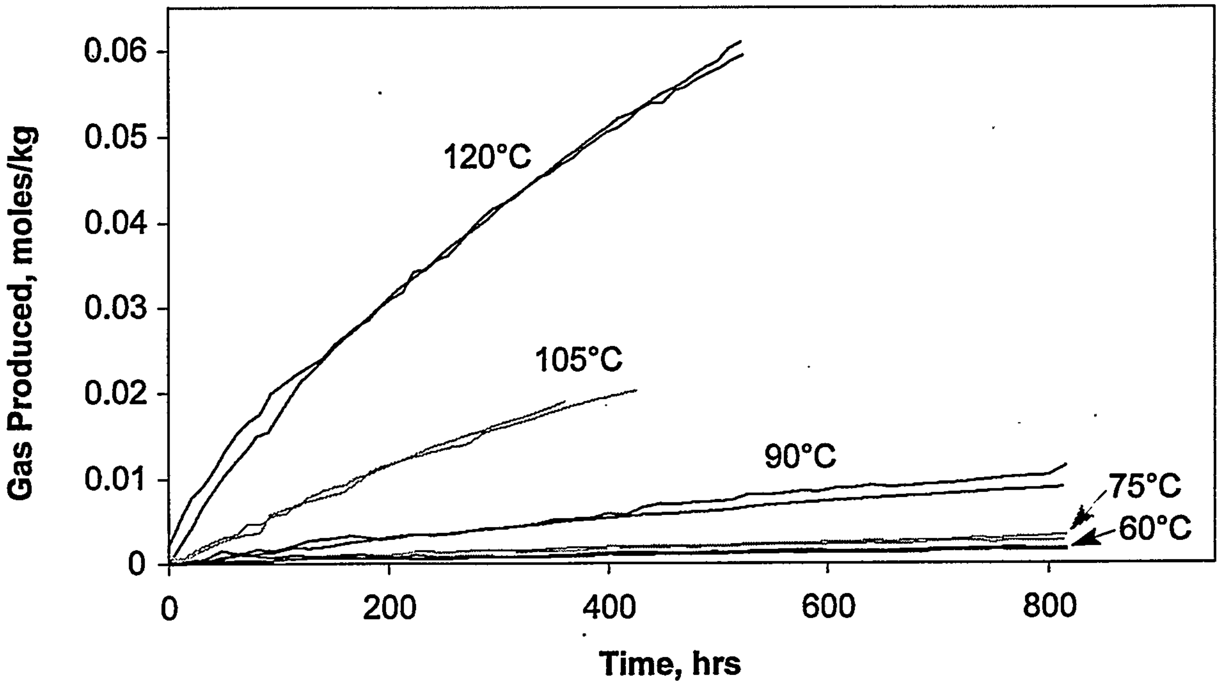

Figure 7. Gas Production in Duplicate Systems from Tank 241-SY-103 Convective Layer (gas generation was performed at 60, 75, 90, 105, and 120°C)

Table 3. Total Gas Generation Rates (mol/kg/day) and Reaction Times (hr) at Various Temperatures (rates calculated from pressure increase data)

	60°C			75°C			90°C	
Run	Rate	Time	Run	Rate	Time	Run	Rate	Time
1a	6.4E-5	331	3a	8.9E-5	329	5a	3.4E-4	331
1b	4.8E-5	340	3b	7.6E-5	340	5b	3.1E-4	339
1c	2.3E-5	145	3c	5.0E-5	145	5c	2.7E-4	145
2a	5.4E-5	331	4a	1.2E-4	331	6a	3.3E-4	331
2b	3.9E-5	340	4b	6.4E-5	340	6b	2.4E-4	337
2c	4.1E-5	145	4c	1.1E-4	145	6c	1.9E-4	144

	105°C			120°C	
Run	Rate	Time	Run	Rate	Time
7a	1.3E-3	160	9a	3.8E-3	186
7b	1.2E-3	162	9b	2.5E-3	66
7c	8.4E-4	103	9c	2.4E-3	139
			9d	1.8E-3	130
8a	1.4E-3	67	10a	3.6E-3	187
8b	1.4E-3	139	10b	2.7E-3	65
8c	1.1E-3	154	10c	2.4E-3	139
			10d	2.0E-3	130

Table 4. Total Moles of Gas Present in Each System at Termination of Gas Generation

Run	60°C	Run	75°C	Run	90°C	Run	105°C	Run	120°C
1a	0.00105	3a	0.00102	5a	0.00109	7a	0.00121	9a	0.00143
1b	0.00104	3b	0.00101	5b	0.00107	7b	0.00115	9b	0.00100
1c	0.00103	3c	0.00098	5c	0.00102	7c	0.00113	9c	0.00117
								9d	0.00114
2a	0.00103	4a	0.00104	6a	0.00107	8a	0.00094	10a	0.00163
2b	0.00102	4b	0.00103	6b	0.00107	8b	0.00103	10b	0.00116
2c	0.00101	4c	0.00101	6c	0.00102	8c	0.00104	10c	0.00133
								10d	0.00133

and moles present at the end of a reaction, while the reaction vessel was maintained at the reaction temperature. The vessel temperature, and thus the vapor pressure of water, are the same at both times for which moles were calculated, so the effect of the water vapor pressure cancels out. The duplicate samples shown in Figure 7 are in fairly good agreement. As can be seen from the data in Table 3, the rate of gas generation tends to decrease from sample "a" to sample "c" (or "d") as the experiment progresses, as expected from the curvature of the plots in Figure 7. The exceptions occur for gas generation from the 60 and 75°C reactions, which appear to be linear over this time frame. This is most likely due to the fact that the reactions had not progressed to near the fraction of completion as the higher-temperature experiments.

The mole percent composition of the gas sampled at the end of each reaction is given in Table 5. This composition data is presented including argon and is also presented normalized to include only the gases generated (excluding argon, shaded grey in Table 5). The composition of gas formed during heating is calculated from the total gas measured in the reaction vessel, by normalizing the data to 100% after removal of the inert gas Argon. For example, if analysis found 80% Ar, 15% N_2O, and 5% H_2, the composition of gas formed would be 75% N_2O and 25% H_2. The most abundant gas generated in Tank 241-SY-103 waste varied with temperature. Generally speaking, nitrogen was the most abundant gas generated at low temperatures, while N_2O dominated at higher temperatures. The oxygen abundance drops as temperature increases in all runs, which is consistent with oxygen being a contaminant, whose concentration is reduced as other gases are formed.

We believe the trace oxygen was a contaminant from gas sampling rather than generated from these tests since under similar reaction conditions, with an atmosphere of 30% oxygen, Tank 241-SY-101 material reacts with O_2 on heating.(a) The oxygen concentration in these experiments is small, ranging from 0.002% to 0.058%. Except for the gas generated at

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(a) Person, J. C. Presentation on November 6, 1995, entitled, *Gas Generation Studies in 101-SY Tank Waste.*

Table 5. Percent Composition of Gas Sampled (including argon), Gas Formed (shaded), and Heating Times for Duplicate Systems at Five Temperatures

Run	Mole Percent of Gas Formed at 60°C										Time, hr.
	Ar	N_2	H_2	N_2O	O_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	
1a	99.54	0.186	0.21	0.054	0.011						331
		40.4	45.7	11.7	2.4						
1b	99.53	0.221	0.139	0.085	0.017	0.003					340
		47.0	29.6	18.1	3.6	0.6					
1c	99.67	0.194	0.053	0.059	0.028						145
		58.8	16.1	17.9	8.5						
2a	99.33	0.288	0.274	0.086	0.024	0.001					331
		43.0	40.9	12.8	3.6	0.15					
2b	99.29	0.32	0.124	0.134	0.033	0.09		0.007			340
		45.1	17.5	18.9	4.6	13		1.0			
2c	99.65	0.207	0.047	0.057	0.033	0.003					145
		59.1	13.4	16.3	9.4	0.9					

Run	Mole Percent of Gas Formed at 75°C										Time, hr.
	Ar	N_2	H_2	N_2O	O_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	
3a	97.3	1.16	0.81	0.69	0.026	0.005					329
		43.0	30.0	25.6	1.0	0.19					
3b	97.5	1.04	0.46	0.87	0.03	0.06		0.006			340
		41.6	18.4	34.8	1.2	2.4		0.2			
3c	99.01	0.438	0.166	0.335	0.034	0.015					145
		44.2	16.8	33.8	3.4	1.5					
4a	97.4	1.19	0.74	0.58	0.055	0.004					331
		45.8	28.5	22.3	2.1	0.15					
4b	97.93	0.92	0.376	0.72	0.039	0.006					340
		44.4	18.2	34.8	1.9	0.3					
4c	99.13	0.388	0.145	0.282	0.04	0.011					145
		44.6	16.7	32.4	4.6	1.3					

Table 5 (contd)

Run	Mole Percent of Gas Formed at 90°C										Time, hr.
	Ar	N_2	H_2	N_2O	O_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{2,4\text{ or }6}$	butadiene	
5a	92.0	2.87	2.07	2.91	0.052	0.006	0.03	0.012	0.016	0.005	331
		35.9	25.9	36.4	0.65	0.08	0.4	0.15	0.20	0.06	
5b	93.0	2.07	1.65	3.13	0.03	0.1	0.016	0.018	0.016		339
		29.6	23.6	44.7	0.43	1.4	0.23	0.26	0.23		
5c	97.0	0.90	0.69	1.26	0.038	0.07	0.032	0.008			145
		30.	23.0	42.0	1.3	2.3	1.1	0.27			
6a	92.0	2.9	2.08	2.86	0.058	0.03	0.02	0.013	0.016		331
		36.3	26.0	35.8	0.73	0.38	0.3	0.16	0.20		
6b	93.4	1.99	1.58	2.94	0.029	0.05		0.016	0.017		337
		30.2	23.9	44.5	0.44	0.8		0.24	0.26		
6c	97.3	0.80	0.67	1.2	0.02			0.007			144
		30.	24.8	44.4	0.74			0.26			

Run	Mole Percent of Gas Formed at 105°C										Time, hr.
	Ar	N_2	H_2	N_2O	O_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{2,4\text{ or }6}$	butadiene	
7a	87.6	3.8	3.52	4.74	0.045	0.15	0.05	0.036	0.025	0.005	160
		30.6	28.4	38.2	0.36	1.2	0.4	0.29	0.20	0.04	
7b	88.9	2.52	3.31	5.0	0.01	0.16	0.045	0.04	0.020		162
		22.7	29.8	45	0.09	1.4	0.41	0.36	0.18		
7c	91.8	1.95	2.4	3.45	0.016	0.35	0.005	0.042	0.012		103
		23.8	29	42.1	0.20	4	0.06	0.51	0.15		
8a	90.3	2.64	3.08	3.7	0.02	0.1	0.07	0.028	0.017	0.005	67
		27.2	31.8	38.1	0.21	1.0	0.7	0.29	0.18	0.05	
8b	85.3	3.44	4.21	6.9	0.01	0.007	0.054	0.039	0.029		139
		23.4	28.6	46.9	0.07	0.05	0.37	0.27	0.20		
8c	84.2	3.68	4.71	7.3	0.011	0.013		0.051	0.031	0.005	154
		23.3	29.8	46.2	0.07	0.08		0.32	0.20	0.03	

Table 5 (contd)

Run	Mole Percent of Gas Formed at 120°C										Time, hr.
	Ar	N_2	H_2	N_2O	O_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{2,4\ \mathrm{or}\ 6}$	butadiene	
9a	61.3	7.42	12.8	16.6	0.018	1.3	0.34	0.216	0.062		186
		19.2	33.1	42.9	0.05	3.4	0.9	0.56	0.16		
9b	84.4	2.69	4.9	6.0	0.005	1.6	0.22	0.146	0.019		66
		17.2	31.4	38.5	0.03	10.3	1.4	0.94	0.12		
9c	73.4	4.65	9.5	11	0.005	0.8	0.31	0.179	0.035		139
		17.5	35.7	41	0.02	3	1.17	0.67	0.13		
9d	76.8	3.95	8	9.46	0.002	1.4	0.21	0.151	0.028		130
		17	34	40.8	0.01	6	0.91	0.65	0.12		
10a	63.4	7.05	12.5	15.8	0.023	0.74	0.26	0.18	0.052		187
		19.3	34.2	43.2	0.06	2.0	0.7	0.49	0.14		
10b	85.8	2.57	4.9	5.9	0.01	0.57	0.14	0.09	0.016		65
		18.1	34.5	41.5	0.07	4.0	1.0	0.63	0.11		
10c	77.3	4.18	8.3	9.7	0.011	0.11	0.179	0.105	0.028		139
		18.4	36.6	42.7	0.05	0.5	0.79	0.46	0.12		
10d	78.6	3.92	8	9.04	0.008	0.15	0.129	0.098	0.024		130
		18.3	37	42.2	0.04	0.7	0.60	0.46	0.11		

60°C where the production of all gases was very small, all nitrogen concentrations are much higher than four times the oxygen concentration (the O_2-N_2 atmospheric ratio); therefore, atmospheric contamination does not significantly affect the nitrogen values reported. Ammonia concentrations in the samples, as measured by mass spectroscopy, are included in Table 5. These are listed as estimates because ammonia adsorbs to the stainless steel walls of the gas sample bottle and ammonia in duplicate runs varies considerably. The concentrations of CO_2, CO, and helium were always less than their detection limits and are absent from all tables.

The composition of the gas samples is shown graphically for the major components in Figure 8. These data are for duplicate systems after the first sample "a" only, which accounts for approximately the first 300-hour reaction time for each run. The gas contains mainly N_2O, H_2, and N_2; the unlabeled region at the top of the Figure 8 represents the minor components, which account for less than 4% of the total gas formed. The percent composition of the minor gases are shown in Figure 9 as a function of reaction temperature.

It is evident from Figures 8 and 9 that the composition of the gas generated varies with reaction temperature. For example, the N_2O-to-N_2 ratio changes from 0.29 (average of duplicate runs) at 60°C to 2.24 at 120°C.

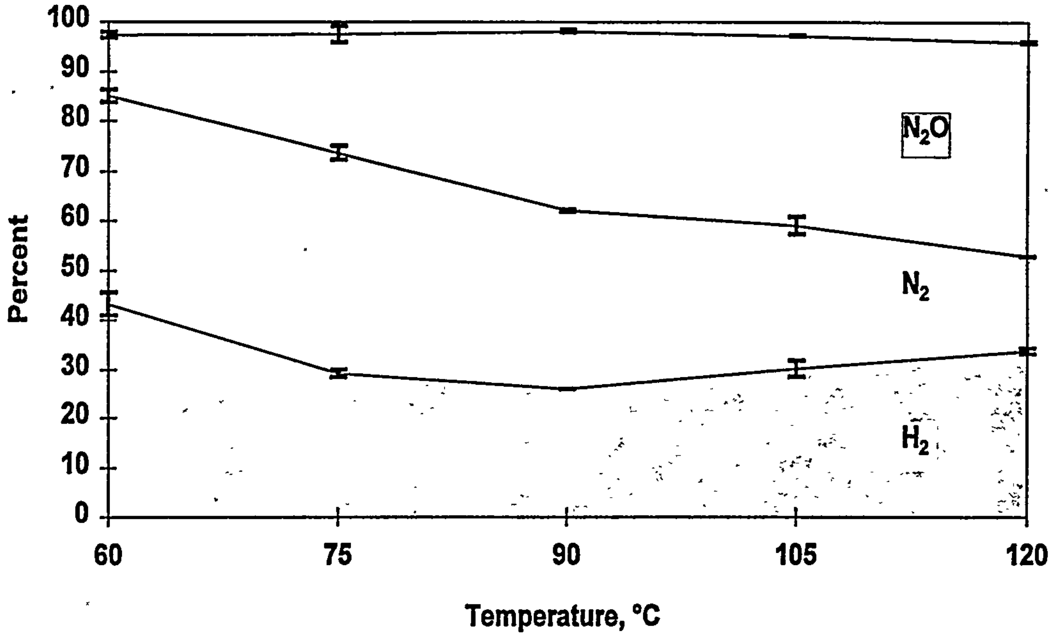

Figure 8. Composition of Major Products as a Function of Temperature from Gas Generation from Tank 241-SY-103

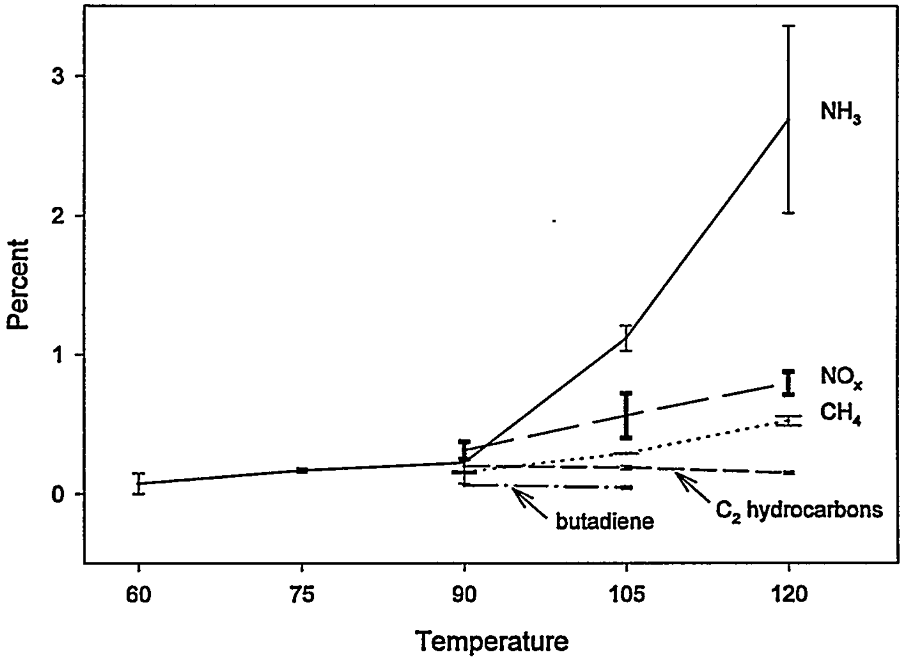

Figure 9. Formation of Minor Gas Components Versus Temperature (error bars give the range for duplicate runs)

Table 6. Ratio of Major Gaseous Products Formed from All Gas Generation Runs (data are averaged from duplicate runs)

60°C Gas Generation Ratios (Runs 1 and 2)

	H_2/N_2	N_2O/N_2	H_2/N_2O
Sample a	1.04	0.29	3.54
Sample b	0.51	0.40	1.28
Sample c	0.25	0.29	0.86

75°C Gas Generation Ratios (Runs 3 and 4)

	H_2/N_2	N_2O/N_2	H_2/N_2O
Sample a	0.66	0.54	1.22
Sample b	0.43	0.81	0.53
Sample c	0.38	0.75	0.50

90°C Gas Generation Ratios (Runs 5 and 6)

	H_2/N_2	N_2O/N_2	H_2/N_2O
Sample a	0.72	1.00	0.72
Sample b	0.80	1.49	0.53
Sample c	0.80	1.45	0.55

105°C Gas Generation Ratios (Runs 7 and 8)

	H_2/N_2	N_2O/N_2	H_2/N_2O
Sample a	1.05	1.32	0.79
Sample b	1.27	1.99	0.64
Sample c	1.26	1.88	0.67

120°C Gas Generation Ratios (Runs 9 and 10)

	H_2/N_2	N_2O/N_2	H_2/N_2O
Sample a	1.75	2.24	0.78
Sample b	1.86	2.26	0.82
Sample c	2.01	2.34	0.86
Sample d	2.03	2.35	0.87

Although this change may be partly due to a change in reaction type with temperature, it is also a result of a change in the relative concentrations of reactants. This can be seen in Table 6, which shows that the composition changes considerably between samples "a" and "b." Samples "b" and "c" (and "d") are nearly identical for the 90, 105, and 120°C systems, suggesting that some especially reactive component has been used up by the end of the first sampling period (approximately the initial 300 hours) at these higher temperatures.

3.2 Rates of Gas Generation from Tank 241-SY-103 Convective Layer

Determining he rate of gas generation from Tank 241-SY-103 as a function of temperature is a primary goals of this work. The rate of total gas generated from Tank 241-SY-103 waste is given in Table 3 as a function of temperature. These gas generation rates were measured using an increase in total moles based on pressure rise data. The rates can also be determined independently using gas composition data according to the following formula:

$$\text{Rate} = \text{(moles of gas in system at end of run)*} \\ \text{(1-(mole \% Ar/100))/(sample mass, kg)/(heating time, days)} \qquad (1)$$

The rate of formation of each component of the gas, from gas composition data (Eq. 1), is given in Table 7. The total rates, calculated from a sum of all the component gases generated, are also given in this table. A comparison of total rates found by the two methods (based on pressure rise data and on composition data) is given in Figure 10. In this figure, all the values would lie on the solid line (slope = 1) if agreement between these two methods were exact.

The rate of generation of the major gas components in Table 7 is also shown graphically in Figure 11 for the major components. As expected, the rate generation of each gas component increases with temperature. It is interesting to note, however, that the relative rates of gases generated at various temperatures are not constant. The gas composition for each reaction is different at various temperatures. As can be seen in Figure 8, the relative concentration of nitrous oxide increases with increasing temperature (from 60 to 120°C). Over the same temperature range, the nitrogen component decreases significantly. The relative concentration for hydrogen production is fairly constant over the entire temperature range from 60 to 120°C in these figures. The consequence of changes in relative concentrations of gases is seen in differences in activation energies for the production of these gases, as discussed in Section 3.3

The data are randomly distributed above and below the line for the data at 75, 90, 105, and 120°C in Figure 12. At 60°C, the values of the gas generation rates from the pressure rise data are higher than the values form gas generation rates from the gas composition data. These higher values are probably related to the uncertainty in measuring a small difference between large numbers, that is, a small increase in moles of gas generated compared with the total moles of inert gas originally present in the reaction vessel. Rates from gas composition data are expected to be more accurate than rates from the increase in moles based on pressure rise, especially at low temperatures.

Table 7. Individual and Total Formation Rates from Each Gas Generation Reaction

60° Gas Generation Rates, mol/kg/day

Run	N_2	N_2O	H_2	NH_3 (est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	TOTAL
1a	6.4E-6	1.9E-6	7.2E-6						1.6E-5
1b	7.4E-6	2.8E-6	4.6E-6						1.5E-5
1c	1.5E-5	4.6E-6	4.1E-6						2.6E-5
2a	9.6E-6	2.9E-6	9.1E-6	3.3E-8					2.2E-5
2b	1.0E-5	4.3E-6	4.0E-6	2.9E-6		2.3E-7			2.3E-5
2c	1.6E-5	4.3E-6	3.5E-6	2.2E-7					2.6E-5

75° Gas Generation Rates, mol/kg/day

Run	N_2	N_2O	H_2	NH_3(est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	TOTAL
3a	3.9E-5	2.3E-5	2.7E-5	1.7E-7					9.0E-5
3b	3.3E-5	2.8E-5	1.5E-5	1.9E-6		1.9E-7			7.8E-5
3c	3.2E-5	2.4E-5	1.2E-5	1.1E-6					7.1E-5
4a	4.0E-5	2.0E-5	2.5E-5	1.3E-7					8.7E-5
4b	3.0E-5	2.3E-5	1.2E-5	1.9E-7					6.7E-5
4c	2.9E-5	2.1E-5	1.1E-5	8.2E-7					6.5E-5

90° Gas Generation Rates, mol/kg/day

Run	N_2	N_2O	H_2	NH_3(est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	TOTAL
5a	1.0E-4	1.0E-4	7.3E-5	2.1E-7	1.1E-6	4.2E-7	5.6E-7	1.8E-7	2.8E-4
5b	7.0E-5	1.1E-4	5.6E-5	3.4E-6	5.4E-7	6.1E-7	5.4E-7		2.4E-4
5c	6.8E-5	9.5E-5	5.2E-5	5.3E-6	2.4E-6	6.0E-7			2.3E-4
6a	1.0E-4	9.9E-5	7.2E-5	1.0E-6	7.0E-7	4.5E-7	5.6E-7		2.8E-4
6b	6.8E-5	1.0E-4	5.4E-5	1.7E-6		5.4E-7	5.8E-7		2.3E-4
6c	6.0E-5	9.1E-5	5.1E-5			5.3E-7			2.0E-4

105° Gas Generation Rates, mol/kg/day

Run	N_2	N_2O	H_2	NH_3(est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	TOTAL
7a	3.1E-4	3.8E-4	2.8E-4	1.2E-5	4.0E-6	2.9E-6	2.0E-6	4.0E-7	1.0E-3
7b	1.9E-4	3.8E-4	2.5E-4	1.2E-5	3.4E-6	3.0E-6	1.5E-6		8.4E-4
7c	2.3E-4	4.0E-4	2.8E-4	4.1E-5	5.8E-7	4.9E-6	1.4E-6		9.6E-4
8a	4.0E-4	5.6E-4	4.6E-4	1.5E-5	1.1E-5	4.2E-6	2.6E-6	7.5E-7	1.5E-3
8b	3.7E-4	7.4E-4	4.5E-4	7.5E-7	5.8E-6	4.2E-6	3.1E-6		1.6E-3
8c	3.0E-4	5.9E-4	3.8E-4	1.0E-6		4.1E-6	2.5E-6	4.0E-7	1.3E-3

120° Gas Generation Rates, mol/kg/day

Run	N_2	N_2O	H_2	NH_3(est.)	NO_x	CH_4	$C_2H_{24\ or\ 6}$	butadiene	TOTAL
9a	6.1E-4	1.4E-3	1.1E-3	1.1E-4	2.8E-5	1.8E-5	5.1E-6		3.2E-3
9b	4.3E-4	9.7E-4	7.9E-4	2.6E-4	3.5E-5	2.4E-5	3.1E-6		2.5E-3
9c	4.2E-4	9.9E-4	8.6E-4	7.2E-5	2.8E-5	1.6E-5	3.2E-6		2.4E-3
9d	3.7E-4	8.8E-4	7.4E-4	1.3E-4	2.0E-5	1.4E-5	2.6E-6		2.2E-3
10a	6.6E-4	1.5E-3	1.2E-3	6.9E-5	2.4E-5	1.7E-5	4.9E-6		3.4E-3
10b	4.9E-4	1.1E-3	9.4E-4	1.1E-4	2.7E-5	1.7E-5	3.1E-6		2.7E-3
10c	4.3E-4	9.9E-4	8.5E-4	1.1E-5	1.8E-5	1.1E-5	2.9E-6		2.3E-3
10d	4.3E-4	9.9E-4	8.7E-4	1.6E-5	1.4E-5	1.1E-5	2.6E-6		2.3E-3

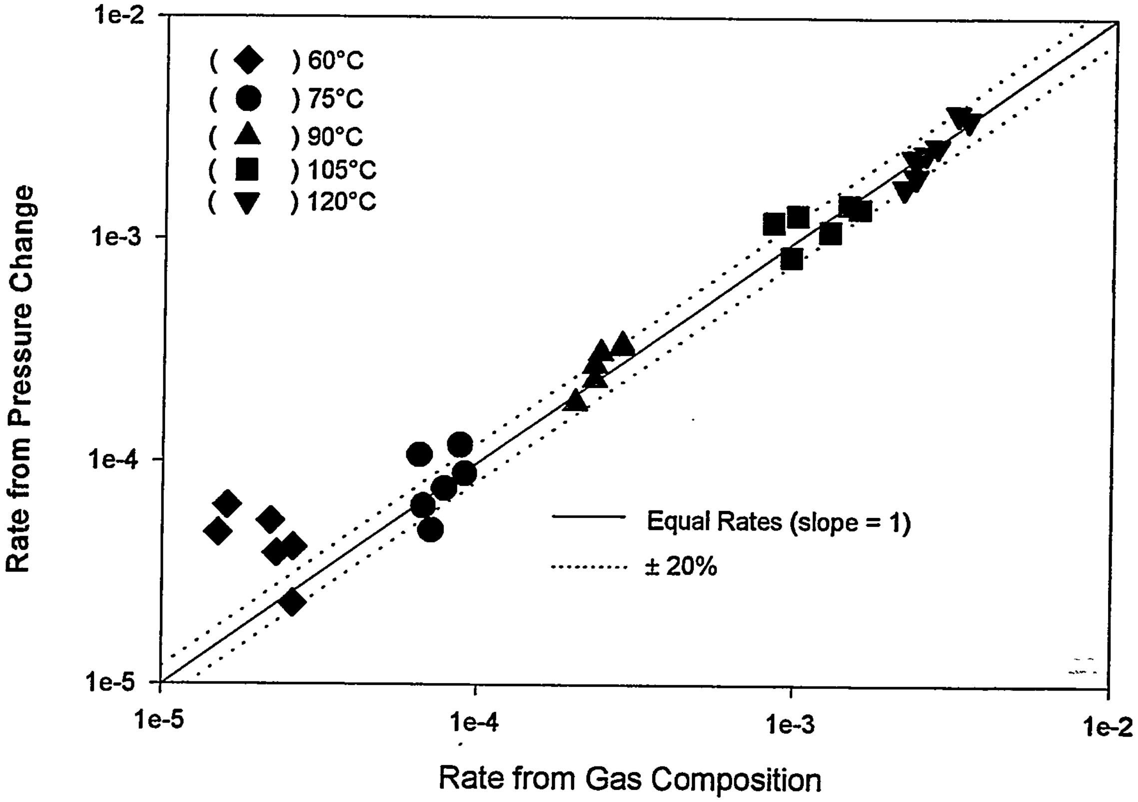

Figure 10. Comparison of Rates (mole/kg/day) Determined from Increase in Moles and Percent Composition.

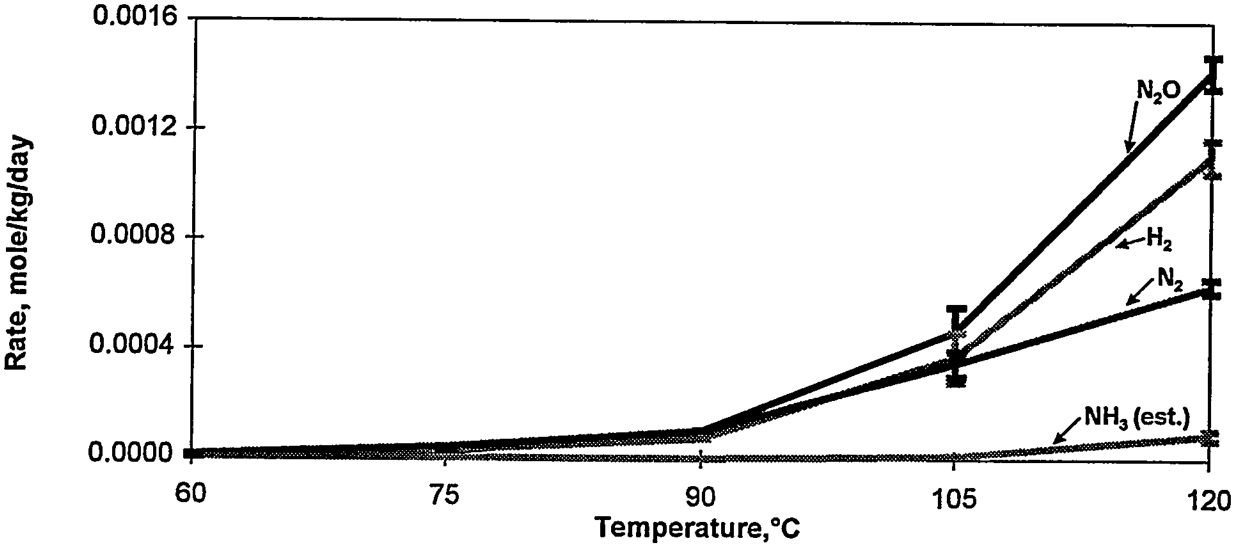

Figure 11. Rate of Formation of Major Gas Components Versus Temperature (error bars give the range for duplicates

3.3 Activation Energy for Gas Generation from Tank 241-SY-103

The activation energy for the initial rate of gas formation for each gas reaction system was estimated from the gas composition and generation data for sample "a" from each run (approximately the initial 300-hour reaction time). An Arrhenius plot of those data is shown in Figure 12. The activation energy for total gas formation is found to be 94 ± 6 kJ/mole (95% confidence level).

Based on the rate of formation of each component gas in the gas generation systems, Arrhenius plots for the major components (H_2, N_2, and N_2O) are shown in Figure 13. The activation energy (E_a) for formation of these components are 80 ± 8 kJ/mole (95% confidence interval) for N_2, 90 ± 9 kJ/mole for H_2, and 116 ± 9 kJ/mole for N_2O. Activation energies for N_2 and H_2 are not significantly different from one another. The activation energy for N_2O is significantly different from the other major components, even at the 99.5% confidence level.

The rate constant for the formation of gas can be calculated at a particular temperature according to Equation 2:

$$k = A^*\exp[-E_a^*1000/RT] \quad (2)$$

where E_a has units of kJ/mole, A is the pre-exponential factor, R is the gas constant, 8.314 J/K-mol, and T is temperature (K). The pre-exponential factors are found to be 3E+07 for N_2, 9E+08 for H_2, 4E+12 for N_2O, and 1E+10 mole/kg/day for the overall reaction. (Ninety-five-percent confidence intervals for these numbers are ± two orders of magnitude. For N_2, for example, the confidence interval for the pre-exponential factor is between 2E+6 and 5E+8 mol/kg/day.)

The observed rate of hydrogen formation in Tank 241-SY-103 has been estimated (Wilkins 1995) to be 9.0 ft^3 H_2/day (6.6 ft^3 H_2/day exiting the tank between events, and 2.4 ft^3 H_2/day that accumulates and is released during events). Assuming this gas is at 80°F and one atmosphere gives an observed rate of 10 mol H_2/day from the entire tank. Since the convective layer accounts for 48% of the material in the tank, the expected rate of formation from just the convective layer would be 4.8 mol H_2/day, assuming the formation rate of H_2 is the same in both the convective and nonconvective layers.

Hydrogen generation rates for the convective layer of Tank 241-SY-103 can be estimated from the results of laboratory tests and compared with those estimated from tank behavior. At 89°F (31.7°C), a hydrogen formation rate of 3.3 X 10^{-7} mol/kg waste/day is obtained from Eq. (2), using Arrhenius parameters given above (95% prediction interval: $-15.698 < \ln \text{rate} < -14.138$). Assuming that the mass of the convective layer is 2.05 million kg, a rate of 0.67 mol hydrogen/day is obtained (95% prediction interval: $0.31 < \text{rate} < 1.48$). Thus, our hydrogen formation rate estimate derived from laboratory experiments accounts for between 6 and 31%of the 4.8 mol/day estimate from tank observations.

The contribution of radiolytic gas generation can now be assessed and compared with the thermal gas generation measured above. The G-value for the production hydrogen from water radiolysis has been established for simulated wastes with similar composition to Tank 241-SY-103 waste to be 0.03 molecules/100ev (Meisel et al. 1993). This value yields a radiolytic hydrogen production rate of 9×10^{-8} mol/kg-day from these samples based on a self-radiolysis dose rate of 119 R/hr. The radiolytic component of hydrogen gas generation is

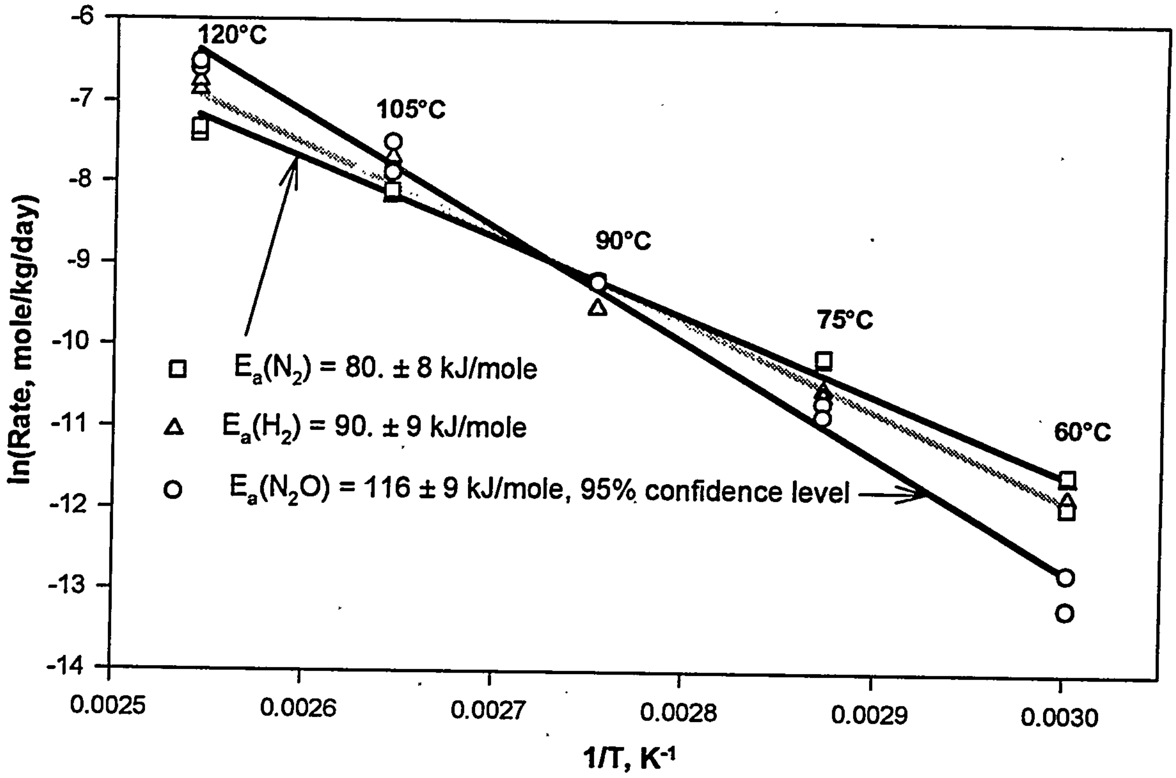

Figure 12. Arrhenius Plot of Rates of Formation of Major Gas Components (the activation energy was calculated from the slope of the least-squares fit line)

approximately 1 to 2% of the total gas generation measured at 60°C. The radiolytic component for hydrogen generation is insignificant for those temperatures higher than 60°C. The importance of the small contribution of the radiolytic contribution at the temperatures of gas generation experiments is that we can assume the gas generation is all coming from the thermal reaction. Therefore, the calculated activation energies can be used to accurately extrapolate a "thermal-only" gas generation rate at the lower tank temperature of 31.7°C.

The Tank 241-SY-103 radiolytic hydrogen gas generation should be estimated for the tank dose rate of 444 R/h, not the test sample self-radiolysis dose rate of 119 R/h used above. This gives a radiolytic contribution (water radiolysis only) of 9e-8 x 444/119 = 3.4 X 10^{-7} moles H_2/kg waste/day. This is approximately equal to the thermal estimate of 3.3 X 10^{-7} moles H_2/kg waste-day. We might thus expect that radiolysis and thermal gas generation are both important at low temperatures in Tank 241-SY-103.

4.0 Summary

This report addresses the gas generation capacity of the waste from the convective layer of Tank 241-SY-103, a waste tank listed on the Flammable Gas Watch list due to its potential for flammable gas accumulation above the flammability limit (Hanlon 1993).

The gas reaction system developed in earlier work using simulated waste was modified to accommodate the needs of operations within the hot cell facility used for the actual waste samples in this study. Verification tests designed to challenge the systems ability to measure the quantity of gas at various temperatures and pressures similar to those anticipated within this study demonstrated that the quantity of gas was accurately modeled using the Ideal Gas Law and that the temperatures, volumes, and pressure of each system were accurately assessed. In all, 12 independent reaction systems (10 in use, two spares) were fabricated and tested prior to use with actual waste. In all cases, the ability of each system to measure the quantity of gas within the system was reproducible and excellent.

The waste samples from Tank 241-SY-103 used in this study are measured under two conditions, first, with externally applied heat, and second, with externally applied heat and radiation (^{137}Cs capsule). In the thermal experiments discussed in this report, the self radiolysis of the sample is not negligible and must be considered to understand the total gas generation. The self-dose rate of the actual waste was calculated based on the known inventory of radionuclides and chemical composition of the waste as well as the geometry and construction of the reaction vessel. The calculated self dose rate is 119 rad/hr averaged over the entire sample, assuming a 14.7 mL sample in a flat-bottomed stainless (304) steel vessel. More than 99% of the absorbed radiation dose comes from the decay of ^{137}Cs (beta and gamma). The second phase of the work, in which the waste is introduced to an external gamma field, is currently being investigated, and results will be published in a subsequent report.

A main objective of this work is to establish the identity and stoichiometry of degradation products formed in actual tank wastes by thermal and radiolytic processes as a function of temperature. The focus of the gas generation tests on Tank 241-SY-103 samples is first on the effect of temperature on the composition and rate of gas generation. The generation rate of N_2, N_2O, and H_2 (and several minor components) increases with temperature. The relative rates of gases generated at various temperatures is not constant, however; the gas composition for each reaction is different at various temperatures. The relative concentration of nitrous oxide increases with increasing temperature (from 60 to 120°C). The nitrogen component decreases significantly over this temperature range. The relative concentration for hydrogen production is fairly constant over the entire temperature range from 60 to 120°C. The consequence of changes in relative concentrations of gases will be seen in differences in activation energies for the production of these gases.

Arrhenius treatment of the rate data revealed activation parameters for the gas generation from Tank 241-SY-103. The activation energy for total gas formation is found to be 94 ± 6 kJ/mole (95% confidence level). Based on the rate of formation of each component gas in the systems, activation energies were calculated. The activation energies (E_a) for formation of these components are 80 ± 8 kJ/mole (95% confidence interval) for N_2, 90 ± 9 kJ/mole for H_2, and 116 ± 9 kJ/mole for N_2O.

The task for measuring gas generation from the waste from Tank 241-SY-103 is a continuing project. The second phase of this work is the study of the gas generation capacity of Tank 241-SY-103 waste in the presence of an external gamma source. This work is being performed during the last half of FY 1996. In addition to the gas generation from the thermal and radiolytic treatment of the tank waste, the organic components of the waste are being analyzed. The waste is being analyzed for specific organic components before and after heating and radiolysis to help identify the organic species responsible for gas generation. By following the specific organic species present and their concentration changes as a function of heating and irradiation, together with the information of the gases formed during the heating and irradiation treatments, an understanding of the organics responsible for gas generation is possible. The gamma-assisted gas generation and organic analysis of the waste will be reported in a subsequent document.

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Appendix

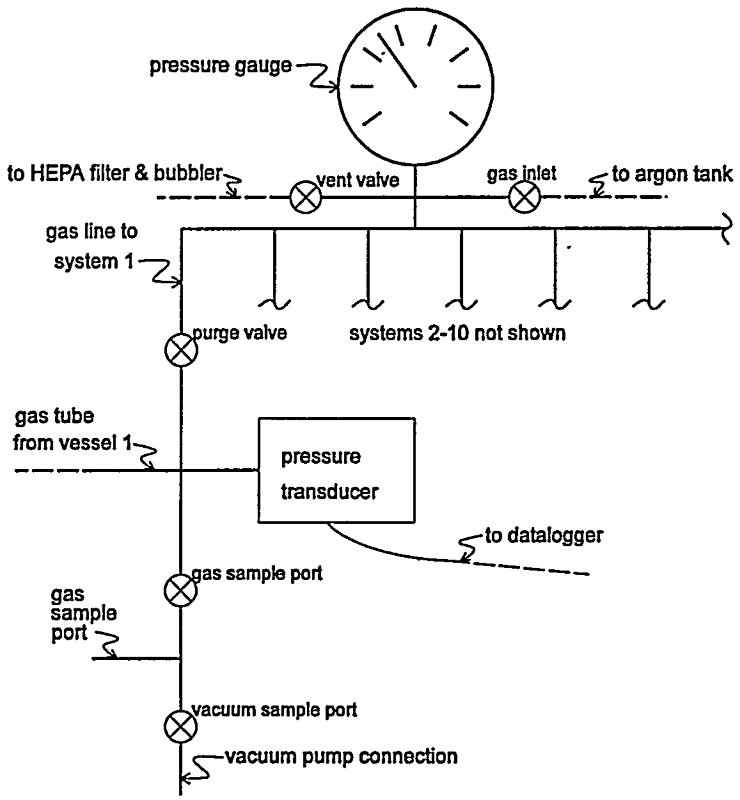
Procedure: Reaction Startup and Gas Collection

Procedure: Reaction Startup

This procedure is for starting a reaction in duplicate.

Vessel numbers [1-10]: _____ Operator: ____________________ Date: _________

Schematic of Pressure Manifold



__1. Confirm that all connections have been made: thermocouples, heater power, gas transfer line. Also confirm that insulation has been placed around the top of the vessels. The vessels should have been leak tested.

__2. Have the computer program graphterm display and graph the gas and liquid temperatures and the pressure associated with each vessel. (Adjust the graph scale. Confirm that the selected temperatures and pressures are actually on the graph.)

__3. Open the valve on top of the argon tank.

__4. Vent any gas in the vessels:
    Close the gas inlet valve on the manifold
    Open the vent valve (to bubbler)
    Open the purge valve for both vessels
    Wait until the bubbler stops bubbling (about 5 minutes).

__5. Purge each vessel:
    Close the vent valve
    Open the gas inlet valve (gauge on manifold should read about 40 psig)

Wait 5 minutes for the gas to be transferred to the reaction vessels.
Close the gas inlet valve
Open the vent valve--wait until the bubbler stops bubbling
Close the vent valve
Close the purge valve for both vessels

__6. Heat the vessels
Turn on the heaters to be used.
Set the over-temp. protection controller to 70° (press knob in to set).
Set the heater controller 2 or 3 degrees above the current temperature.
To change set point 1, press the Index button once. The display will show "sp1". Change the set point with the arrow buttons. Press enter

The temperature will considerably overshoot the set point, which is why the set point is not initially set at 60°.
Set the over-temp. protection controller to 70°_(press knob in to set).
Press the reset button so the yellow light goes out.
When 60° is reached, leave at that temperature for at least one hour.

Set point that gave a liquid temperature of 60°: ______

Time 60° reached: _________

__7. Cool down:
Turn the heater controller off.

Time cool down started: _________

Let cool until the liquid temperature reaches 10° above the hot cell temperature (about 45 minutes)

__8. Repeat steps 4 and 5.

__9. Repeat steps 4 and 5 again.

__10. Vent any gas in the vessels:
Close the gas inlet valve
Open the vent valve
Open the purge valve for both vessels
Wait until the bubbler stops bubbling (about 5 minutes).
Close the vent valve
Close the purge valve for both vessels

__11. Heat to reaction temp.:
Set the over-temp. protection controller to 10° above desired temperature.
Set the heater controller to the desired temperature as in step 6.

Final reaction temperature of liquid: _________ Set point: _________

Time reached: _________

__12. Close the valve on top of the argon tank.

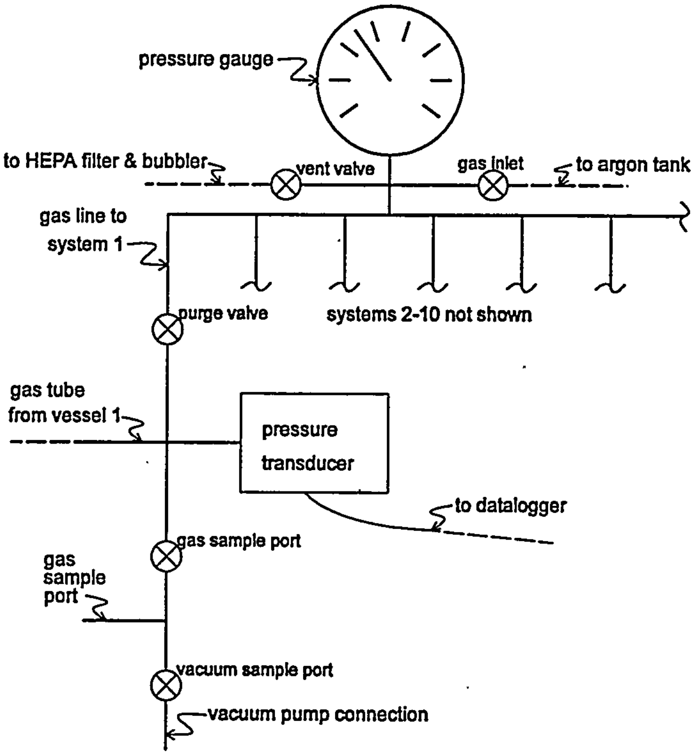
Procedure: Collecting Gas Samples

Vessel number [1-10]: _____ Operator: __________________ Date: ________

Gas Sample Bottle I.D.: ____________

At this point one of the reaction vessels attached to the gas manifold has been warmed up, and is under a pressure of argon plus any gases generated in the experiment. A vacuum pump with a HEPA filter in the inlet side will be used.

Schematic of Pressure Manifold



__1. Record the pressure and manifold temperature in the logbook. Turn off the heat and wait until the vessel is no more than 5°C warmer than the hot cell.

__2. Connect the gas sample container to the gas sample port.
    The gas sample port valve must be closed.
    Remove the plug in the port.
    Insert the end of the gas sample bottle onto the port. An air-tight seal is essential to prevent contamination.
    Leave the valve on the container closed.

__3. Attach the vacuum pump to the vacuum sample port.
    Remove the plug in the port.
    Attach the pump so the HEPA filter is between the pump and the port.

__4. Purge the line. (The gas sample bottle is provided already evacuated by Milt Goheen, 325 building.)

Close (if open) the purge valve.
Turn on the pump. A vacuum of 100 milliTorr should be obtained.
Open the vacuum sample port valve. Leave open for 5 minutes.
Close the vacuum sample port valve.
Disconnect and turn off the pump. (Pump should be disconnected when not running so that the pump oil isn't sucked back into the lines.)

__5. Collect the gas sample.

Open the gas sample valve (on the manifold).
Open the gas sample bottle valve (on the bottle).
Wait 5 minutes while the gas flows through the lines.
Close the gas sample bottle valve.
Close the sample port valve.
Open and close the vacuum sample port valve (This releases the vacuum so the sample bottle can be easily removed).
Remove the gas sample bottle.
Replace the plug in the gas sample port.
Replace the plug in the vacuum sample port.

__6. Record the final pressure and manifold temperature in the log book.

__7. Have an RCT swab the plug to which the gas sample bottle was attached. The swab(s) will immediately be tested for radiation.

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