**Thermal and Combined Thermal and
Radiolytic Reactions Involving
Nitrous Oxide, Hydrogen, and
Nitrogen in the Gas Phase;
Comparison of Gas Generation Rates in
Supernate and Solid Fractions of
Tank 241-SY-101 Simulated Waste**

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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 simulated waste mixtures. Work described in this report was conducted at Pacific Northwest Laboratory (PNL)^(a) for the Flammable Gas Safety Project, the purpose of which is to develop information needed to support Westinghouse Hanford Company (WHC) in their 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 PNL, using simulated wastes, and to studies being performed at WHC using actual wastes.

Described in this report are 1) the results of tests to evaluate the rates of thermal and combined thermal and radiolytic reactions involving flammable gases, and 2) the results of experiments intended to compare gas generation rates in a homogeneous liquid with those in a heterogeneous slurry. Flammable gases generated by the radiolysis of water and by the thermal and radiolytic decomposition of organic waste constituents may themselves participate in further reactions. Examples include the decomposition of nitrous oxide to yield nitrogen and oxygen, the reaction of nitrous oxide and hydrogen to produce nitrogen and water, and the reaction of nitrogen and hydrogen to produce ammonia. The composition of the gases trapped in bubbles in the wastes therefore may change continuously as a function of the time that the gas bubbles are retained. It has often been assumed, although not demonstrated, that the rates of flammable gas generation in the convecting liquid layer and nonconvecting settled solids layer in Hanford double-shell waste tanks are approximately equal. Factors that could lead to different gas generation rates in the two layers include different water content, different concentrations of organic waste components, and catalysis by solid phases.

Gas Reactions under Thermal and Combined Thermal and Radiolytic Conditions: The decomposition of nitrous oxide, reactions between nitrous oxide, and reactions between nitrogen and hydrogen under thermal and combined thermal and radiolytic conditions were investigated in the temperature range of 60 to 150°C. Radiation doses ranged from 0 to more than 100 Mrad (⁶⁰Co), while reaction times extended to 500 hours. Reactions were performed in stainless steel vessels that allowed continuous monitoring of gas pressures. Gas compositions were evaluated using mass spectrometry and infrared spectrometry. Simulated waste mixtures were excluded from these tests.

The primary radiolytic/thermal products of nitrous oxide decomposition were nitrogen, oxygen, and nitrogen dioxide. Under thermal-only conditions, the extent of nitrous oxide decomposition was too small to be observable. Under combined thermal and radiolytic conditions, $G(-N_2O)$ was determined to be 12 molecules/100 eV, in good agreement with literature values. No temperature dependence of $G(-N_2O)$ was apparent from 60 to 150°C. Nitrogen dioxide yields decreased with increasing temperature, while nitrogen yields increased with increasing temperature. Assuming a gamma dose

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rate of 1000 R/h in the actual wastes, and assuming that nitrous oxide composes $\approx 30\%$ of the gases trapped in the nonconvecting layer, it is estimated that $\approx 1\%$ of the retained nitrous oxide could be consumed by these radiolytic reactions per year.

The products of nitrous oxide reactions with hydrogen under thermal and combined thermal and radiolytic conditions were nitrogen, oxygen, and ammonia. Nitrous oxide consumption under thermal-only conditions was considerably greater with hydrogen present than in the absence of hydrogen. This is consistent with the recent findings of Hertzberg and Zlochower (1994), who showed that even very small additions of hydrogen to nitrous oxide are effective in catalyzing nitrous oxide decomposition reactions. Under combined thermal and radiolytic conditions in the presence of hydrogen, $G(-N_2O)$ was determined to be 30 molecules/100 eV, approximately 2.5 times greater than that determined in the absence of hydrogen.

Ammonia was the principal product of the thermal and combined thermal and radiolytic reactions of nitrogen and hydrogen. Radiolytic ammonia yields showed a strong inverse relation with radiation dose. For low radiation doses, $G(NH_3)$ was nearly 1 molecule/100 eV, in good agreement with literature values. However, this yield decreased to approximately 0.01 molecules/100 eV for doses greater than 10 Mrad. From literature results, the value of $G(-NH_3)$ is known to be as much as a factor of ten greater than $G(NH_3)$, depending on temperature and gas partial pressures. As the concentration of NH_3 increased in the gas mixture, so did the relative importance of ammonia decomposition back to nitrogen. Radiolysis of ammonia in the gas phase may be one important means by which the ultimate concentration of ammonia is limited in Hanford Site wastes.

The gas phase reactions were performed with no simulated wastes (solids or liquids) present. Important reactions may occur at the liquid/gas or solid/gas interface. Studies are continuing in FY 1995 to assess the influence of gas reactions in contact with simulated waste liquids and solids.

Comparison of Gas Generation in Homogeneous Liquid and Centrifuged Solids Fraction of a Simulated Waste Mixture: Nearly identical overall rates of gas generation were obtained from the homogeneous liquid fraction and centrifuged solids fraction of a simulated waste under thermal and combined thermal and radiolytic conditions, when corrected for the organic content of the two fractions. The simulant in these tests contained trisodium HEDTA as the sole organic constituent. Trisodium HEDTA was partitioned between the two fractions in a manner roughly proportional to the water content. While the total quantities of gases produced were similar, there were differences in the stoichiometry of the product. Gases produced by the centrifuged solids fraction contained higher nitrogen concentrations than did mixtures produced by the homogeneous liquid. Catalysis of nitrous oxide decomposition reactions by solid phases may have been responsible for these differences.

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1.0 Introduction

This report summarizes progress in evaluating reactions by which flammable gases are generated in Hanford double-shell waste tanks, from studies using simulated waste mixtures on a laboratory scale. Two topics are presented in this report: 1) gas reactions under thermal and combined thermal and radiolytic conditions, and 2) comparisons of flammable gas generation in heterogeneous and homogeneous simulated waste slurries. Work described in this report was conducted for the Flammable Gas Safety Program at Pacific Northwest Laboratory (PNL), whose purpose is to develop information needed to support the interim safe storage of nuclear and chemical wastes at the Hanford Site. Additional studies using simulated wastes are being conducted at the Georgia Institute of Technology (GIT) under a subcontract to PNL.

1.1 Gas Reactions Under Thermal and Combined Thermal and Radiolytic Conditions

Among the gaseous products of chemical and radiolytic reactions that occur in the wastes stored in Hanford double-shell tanks are hydrogen, nitrous oxide, nitrogen, ammonia, and methane (Ashby et al. 1992; Babad et al. 1991, 1992; LANL 1994). From studies using simulated wastes, the kinetics of formation and the stoichiometry of these gaseous products have been shown to be sensitive to the composition of the waste mixture (Delegard 1980; Jansky and Meissner, in Reynolds et al. 1991; Ashby et al. 1992, 1993, 1994a,b; Meisel et al. 1991, 1992, 1993; Bryan et al. 1992, 1993; Bryan and Pederson 1994). Nitrite, hydroxide, and aluminate ion concentrations are critical factors affecting gas generation behavior; other important factors include the identity and concentration of organic waste components, temperature, the presence and concentration of transition metal salts and chloride ions, and radiation dose/dose rate.

Recent results have shown that gas products may participate in additional chemical reactions (Ashby et al. 1994b; Bryan and Pederson 1994). Ashby et al. (1994b) have shown that nitrous oxide partially decomposes to nitrogen and oxygen in tests performed under thermal conditions in glass reaction vessels. They attributed nitrous oxide decomposition reactions to catalysis by glass surfaces. Bryan and Pederson (in Strachan and Schulz 1993) also reported that nitrous oxide decomposed in tests with simulated wastes, particularly under radiolytic conditions. The nitrous oxide/hydrogen product ratio thus may be a function of the time that these gases remained trapped in the wastes.

One way that gases are believed to be trapped in Hanford double-shell tank wastes is as bubbles attached to solid particles, the result of relative surface tension forces (Bryan, Pederson, and Scheele 1992). Gas reactions can thus occur within these bubbles, as shown schematically in Figure 1, possibly catalyzed by the inorganic solid surfaces. While the gases may also be dissolved in the liquid, solubilities are expected to be very low in the concentrated wastes (Schumpe 1993; Bryan and Pederson, in Schulz and Strachan 1992; Allemann 1994), except for ammonia (Norton and Pederson 1994). Gases may also be retained in interstitial voids or pockets, as described recently (Gauglitz et al. 1994a, 1994b). Possible gas reactions within the plenum space at the top of the tank are not considered to be important, because the residence time in these well-ventilated tanks is exceedingly short. Displacement of the liquid from the non-convecting layer by formation of gas bubbles will lower the effective cesium

inventory and thus the dose rate. However, this effect will be offset by the relatively low attenuation of gamma radiation in bubbles compared to the liquid, which results in greater contributions to the dose rate to bubbles from more distant cesium. Such effects are believed to be too small to change our conclusions.

In this study, several potential gas reactions have been considered with regard to their effect on flammable gas yields under both thermal and combined thermal and radiolytic conditions. These are 1) decomposition of nitrous oxide, 2) reaction of nitrogen and hydrogen, and 3) reaction of nitrous oxide and hydrogen. Reactions were studied in the temperature range of 60 to 150°C with and without gamma radiation present. The primary products of nitrous oxide decomposition are expected to be nitrogen and oxygen, as discussed above, whereas the product of nitrous oxide and nitrogen reaction with hydrogen should be ammonia.

1.2 Comparison of Gas Generation In Heterogeneous and Homogeneous Simulated Wastes

Bryan and Pederson (1994) reported that gas generation rates from a homogeneous simulated waste, SY1-SIM-93B, was approximately a factor of ten smaller than that obtained for a simulated waste slurry, SY1-SIM-91A. Both simulants contained the principal inorganic components of actual tank wastes: sodium aluminate, sodium nitrite, sodium nitrate, sodium carbonate, and sodium hydroxide. Both also contained identical concentrations of trisodium HEDTA. Differences in rates could not be explained by differences in the concentrations of key simulant components. Results suggested that inorganic solid surfaces enhanced chemical reactions leading to flammable gas production. In this study, the heterogeneous simulant SY1-SIM-91A, containing trisodium HEDTA as the sole organic constituent, was separated into two fractions: settled solids and supernatant liquids. Gas generation rates under thermal and combined thermal and radiolytic conditions were then determined for the two fractions to more directly assess the possible catalytic role of inorganic solid surfaces.

Figure 1. Gas Phase Reactions of Nitrous Oxide and Hydrogen

2.0 Experimental Methods for Gas Measurements and Sample Irradiation

Sample irradiation experiments were performed within the Gamma Irradiation Facility operated by PNL and located in the 3730 Building in the 300 Area. The facility contains 37 stainless steel irradiation tubes positioned in a 7-foot-diameter by 13-foot-8-inch-deep stainless steel tank. Two arrays of ^{60}Co with a combined inventory of 32 kCi are located near the bottom of the tank. For radiation shielding purposes, the tank is completely filled with water; a concrete wall, 3-1/2 feet in height, surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length from 16 to 18 feet and in diameter from 1.8 to 6 inches. The irradiation dose rate of the tubes ranges from 2×10^6 R/h to 2×10^2 R/h. The uniform flux region varies from ~6 inches for the tubes closest to the sources to greater than 12 inches for the tubes farthest from the sources. All flux measurements of the tubes are traceable to the National Bureau of Standards.

Calibration of the ^{60}Co gamma irradiation facility were performed using an ion chamber and thermoluminescent dosimeters (TLDs). The ion chamber measurements were made using a Capintec® PR-06C chamber with built up cap, S/N CIIG 64053, and a Keithly electrometer, S/N 115092. The ion chamber is a transfer standard, which carries a calibration certificate for ^{60}Co from the National Bureau of Standards. The calibration of this chamber was confirmed by direct comparison with a Capintec® PM-30 chamber, which carries a calibration certificate for ^{60}Co from the National Bureau of Standards. The ion chamber calibration measurements were performed in Gamma Access Tube 21 with a chamber centered 6, 8, and 10 inches from the bottom of the tube. Ion chamber calibration results are kept on file within the gamma facility.

TLD exposures were made by placing packets containing three TLDs inside the center of a 33-inch-long by 1.5-inch-diameter plastic (lucite) tube, which has 32 positions at 1-inch intervals. This tube provides electronic equilibrium and reproducible geometry. The lucite tube has three holes drilled through it to allow for insertion of plastic rods to guide the alignment of the TLD to the center of the ^{60}Co exposure tube. The exposure times for the TLDs were controlled and recorded.

The TLDs were calibrated by placing TLD packets in the lucite rod at positions corresponding to the positions of the National Bureau of Standards traceable ion chamber calibrations. A series of TLD exposures for varying times provided data to determine the TLD response versus exposure time data. The results of the TLD measurements were used to calculate the dose rate (R/h) in all the ^{60}Co exposure tubes within the 3730 gamma facility. Current dose rates are adjusted for natural decay of the ^{60}Co source. Sources of error for gamma tube calibration include exposure geometry, ion chamber measurement, TLD response, calibration fit, and source decay errors. The overall average tube calibration uncertainty is estimated to be 6%.

Materials, capsules, and test systems were lowered into the irradiation tubes to the desired flux manually or by using a half-ton crane. They were left in the tubes for a specific amount of time to attain the required exposure. There is no activation associated with the gamma irradiation, so the materials can be transported to other facilities for examination after removal from the tubes.

The stainless steel reaction vessels used in this study were wrapped with heat tape. Temperatures were regulated by temperature controllers monitored by recording thermocouples and a data logger. Pressures of each reaction vessel were measured using pressure transducers connected to the gas manifold line of each reaction vessel. Small-diameter stainless steel tubing connected the reaction vessel to the gas manifold system.

Total moles of gases produced were calculated based on the measured pressure, temperature, and known volume of the gas phase of the reaction vessel. The volume of the reaction vessels were determined gravimetrically by filling with water. The volumes of the pressure sensor, valves, and miscellaneous fittings were determined from pressure/volume relationships using a calibrated gas manifold system.

In virtually all cases, only one sample was run to obtain each point. Each G value reported was a separate, independent experiment, not the same sample analyzed at different times. We assume that the gases were well-mixed, a reasonable assumption. Samples were withdrawn through the capillary line into an evacuated bulb. The volume of the capillary line was small - less than 2 mL, whereas the reaction vessel volume was ≈ 1 liter and the collection bulb volume was ≈ 30 mL. Because gases will move by viscous flow through the capillary tube in this pressure regime, we do not anticipate that significant errors will be introduced by using this procedure.

Analyses to determine the mole percent of the components within the gas phase of each reaction vessel were performed using the Mass Spectroscopy Facility operated by PNL and located in the 325 Building in the 300 Area. The amounts of specific gases generated were calculated from the total moles of gas generated and the mole percent data. We did not directly assess the recovery of ammonia by filling the experimental apparatus with a known concentration of ammonia followed by sample extraction and analysis. As such, our ammonia concentration values may be biased low if some of the ammonia were lost by adsorption on vessel walls. For the gas phase experiments, ammonia concentrations were determined using infrared spectrometry, based on the analysis of standard gas mixtures. Ammonia concentrations in the gas generation section of this report were based on mass spectroscopy results.

G values are calculated by dividing the number of molecules of product formed (or reactant consumed) by the total energy absorbed by all of the gases present in the reaction vessel. We are aware that inerts will affect the rates of radiolytically driven reactions. When we calculate G-values for a particular reaction, energy absorbed by inerts such as argon are included. This energy is transferred to reacting molecules by collisions.

The reaction containers used in this study were stainless steel Parr[®] reaction vessels, approximately 1 L in volume. The vessels were dried at approximately 110°C before filling. Reaction systems (for thermal and thermal-radiolytic reactions) were initially flushed with inert gas by evacuating and purging argon gas through the vessels attached by stainless steel tubing to a gas manifold system at least three times. Reaction systems were then filled with the reaction gas mixture by equilibrating the reaction gas into the evacuated vessels from the gas manifold system simultaneously. The gas pressure in each reaction system was atmospheric at the time the vessel was closed immediately before the start of the experiment. The gas manifold system used to connect multiple reaction vessels and sampling methodology was discussed in detail in an earlier report (Bryan and Pederson 1994).

There may be some effect of the container walls on radiolysis results. We did not conduct tests in different types of vessels to directly evaluate such effects. However, it is noted that reasonably good agreement between G-values reported in the literature and those determined here were obtained for low dose rates for several reactions of interest. Yields tended to decrease with increased absorbed dose, indicating back reactions. Within experimental error, we did not find radiolytic yields that were higher than literature values. As such, container walls did not appear to enhance reaction rates by radiolytic processes. If anything, they suppressed reaction rates.

Analyses of gas generation from repeated experiments provided estimates of errors for determining gas product formation in gas phase reactions and in gas generation from simulated wastes. The relative error for replicate gas samples using the reaction vessels (≈ 1 L capacity) is approximately 5%.

There are several contributors to gas measurement error. Uncertainties in temperature are believed to be the most important. For an activation energy of 25 kcal/mole, approximately that reported for gas generation and related reactions (Delegard 1980, Schmidt et al. 1993; Orth et al. 1993; Meisel et al. 1993; Ashby et al. 1993; Schmidt et al. 1994), a one-degree difference in temperature from 90°C would yield a 10% change in rate, a two-degree difference would yield a 20% change in rate, and a five-degree difference would yield a 60% change. The 1 L reaction vessels were independently temperature controlled and monitored throughout the tests to within $\pm 0.5^\circ\text{C}$ leading to a 5% error because of changes in thermal reaction rates and assuming a 25 kcal/mole activation energy. Other direct contributors to measurement uncertainties are mass spectroscopy analyses and pressure measurements. The precision in mass spectroscopy measurements was approximately 2% while the precision in pressure measurements is approximately 1%. The absolute reaction vessel volume was known to better than 1%, while the quantity of reactants introduced into the reaction vessel was known to better than 0.1% for solid and liquid samples, and 1% for gaseous reactants. The calculated root-mean-square error from all of the contributors to measurement uncertainty is dominated by the estimated temperature contribution and dose rate calibration uncertainty, or 8%. Uncertainties in gas analysis data were also discussed in detail in an earlier report (Bryan and Pederson 1994).

3.0 Reactions Involving Gases

Gases that are generated by thermal and radiolytic processes may themselves participate in further reactions. Such reactions may occur in the gas phase within gas bubbles trapped in the wastes or may be catalyzed by solid surfaces. Dissolved gases, particularly ammonia, may participate in reactions in the liquid phase. The consequences of such reactions are changing gas product distributions as a function of the time that the gases remain held within the wastes. Experiments were performed to assess the extent of three sets of reactions under thermal and combined thermal and radiolytic conditions. These are discussed in the following sections: Section 3.1, Nitrous Oxide Decomposition Reactions; Section 3.2, Reactions of Nitrous Oxide and Hydrogen; and Section 3.3, Reactions of Nitrogen and Hydrogen. Ammonia is one of the principal products of nitrous oxide and nitrogen reactions with hydrogen. A survey of the literature on ammonia decomposition reactions is included in Section 3.4, although no laboratory measurements specifically aimed at ammonia decomposition were conducted in this study.

3.1 Nitrous Oxide Decomposition Reactions

Nitrous oxide decomposition has been observed in gas generation studies with simulated wastes under both thermal and radiolytic conditions (Ashby et al. 1994b; Bryan and Pederson 1994). Enhanced formation of nitrogen gas occurred concurrently with the disappearance of nitrous oxide for long reaction times. Such reactions may be important in determining the final proportion of nitrous oxide that is produced in Hanford Site waste tanks. In Section 3.1.1, the results of measurements to assess the rates of nitrous oxide decomposition as a function of radiation dose and temperature are described. Section 3.1.2 includes a literature review of thermal decomposition mechanisms, both gas phase and surface-catalyzed reactions, and a comparison with present results. Section 3.1.3 addresses radiolytic mechanisms.

3.1.1 Nitrous Oxide Decomposition Experimental Results

Nitrous oxide decomposition reactions were assessed under thermal and combined thermal and radiolytic conditions. Reactions were conducted in stainless steel vessels in the temperature range of 60 to 150°C and gamma radiation doses from 0 to more than 10^8 rad; reaction times extended to approximately 500 hours. The reaction vessels were initially filled with nitrous oxide and argon (nominally 5 mole percent) at one atmosphere total pressure. Gas compositions were analyzed by mass spectrometry before and after the tests.

The extent of nitrous oxide decomposition without gamma ray irradiation was immeasurably small, in the temperature range of 60 to 150°C. Decomposition under radiolytic conditions was apparent, at rates that increased with increased radiation dose. These results are summarized in Table 1 and Figures 2 through 5. The extent of radiolytic decomposition of nitrous oxide showed no discernable temperature dependence.

Although the rate of nitrous oxide decomposition appeared to be independent of temperature for a given radiation dose, the distribution of the products of decomposition was somewhat temperature-sensitive. Products of decomposition were nitrogen, oxygen, and nitrogen dioxide. In particular, nitrogen dioxide concentrations were highest at 60°C and decreased with increased temperature. Nitrogen yields were inversely related to those of nitrogen dioxide, as expected. Calculated radiolytic yields (G-values) for each of the products and the reactant are given in Table 2 for each experimental condition. G-values are also given in Figure 6 as a function of temperature, where the approximately inverse relation between nitrogen and nitrogen dioxide yields can be seen.

When we compare the quantity of nitrous oxide decomposed to the quantity of nitrogen-containing compounds formed (molecular nitrogen plus nitrogen dioxide), we come up short, especially at the lowest temperatures. At the higher temperatures where little nitrogen dioxide was detected, the nitrogen mass balance was quite good. The oxygen mass balance was poor, presumably because it was consumed in reactions with the vessel. Nitrous oxide and nitrogen concentrations are the least subject to bias. Note that at high temperatures (150°C), the quantity of nitrogen formed and nitrous oxide decomposed are equal, within experimental scatter.

Table 1. Gas Phase Composition of Nitrous Oxide Decomposition Reactions

Gas Composition, mol%				conditions	dose (R)
<u>N₂O</u>	<u>N₂</u>	<u>O₂</u>	<u>NO₂</u>		
99.3	0.45	0.077	0.17	60°C	0
98.9	0.67	0.12	0.27	60°C	6.84 × 10 ⁶
92.7	5.71	0.12	1.48	60°C	1.73 × 10 ⁸
99.7	0.11	0.01	0.13	90°C	0
99.4	0.43	0.041	0.14	90°C	6.47 × 10 ⁶
93.8	5.2	0.00	0.66	90°C	1.71 × 10 ⁸
99.97	0.01	0.00	0.05	120°C	0
99.2	0.32	0.02	0.00	120°C	6.47 × 10 ⁶
94.7	4.7	0.00	0.56	120°C	1.71 × 10 ⁸
99.9	0.00	0.00	0.00	150°C	0
99.6	0.41	0.01	0.00	150°C	6.42 × 10 ⁶

Figure 2. Reaction Products of Radiolysis and 60°C Thermolysis of Nitrous Oxide (nitrogen, oxygen, and nitrogen dioxide are observed decomposition products)

Figure 3. Reaction Products of Radiolysis and 90°C Thermolysis of Nitrous Oxide (nitrogen, oxygen, and nitrogen dioxide are observed decomposition products)

Figure 4. Reaction Products of Radiolysis and 120°C Thermolysis of Nitrous Oxide (nitrogen, oxygen, and nitrogen dioxide are observed decomposition products)

Figure 5. Reaction Products of Radiolysis and 150°C Thermolysis of Nitrous Oxide (nitrogen, oxygen, and nitrogen dioxide are observed decomposition products)

Table 2. G-Value Measurements for the Decomposition of N_2O at 60°, 90°, and 120°C

G-Value (molecule/100 eV)				Conditions	Dose
$G(N_2O)$	$G(N_2)$	$G(O_2)$	$G(NO_2)$		
-12.0	7.33	1.3	3.5	60°C	6.84×10^6
- 8.2	6.9	0.055	1.7	60°C	1.73×10^8
-10.6	11.2	1.1	0.5	90°C	6.47×10^6
- 7.5	6.8	0.0	0.7	90°C	1.71×10^8
-12.8	11.0	0.7	-1.8	120°C	6.47×10^6
- 6.5	6.2	0.0	0.7	120°C	1.71×10^8
-12.9	14.5	0.3	0.0	150°C	6.42×10^6
-12	8.1	1.1	3.9	Room temp	$<10^9$ (a)

(a) Literature G-values measured at room temperature, dose $<10^9$ (Harteck and Dondes 1956).

Figure 6. G-Value Measurements for Decomposition of N_2O at Room Temperature, 60, 90, 120, and 150°C at $6.5 \times 10^6 R$ gamma dose (25°C data from Harteck and Dondes [1956])

3.1.2 Thermal Decomposition of Nitrous Oxide: Literature Review and Discussion

Nitrous oxide can thermally decompose either by a complex reaction in the gas phase or via surface-catalyzed reactions. Homogeneous unimolecular gas-phase reactions are expected to be far too slow to be of any importance at tank waste temperatures. Solid surface-catalyzed reactions may result in altered gas product yields in the tank wastes, however.

The kinetics of decomposition of nitrous oxide under thermal conditions in the gas phase has been widely studied (Johnston 1951; Lindars and Hinshelwood 1955a, b; Kaufman et al. 1956; Preston and Cvetanovic 1972). Reactions occur following (Johnston 1951):

Reaction (2) predominates over Reaction (3) below approximately 400K, while the reverse is true above that temperature (Johnston 1951; Kaufman et al. 1956; Preston and Cvetanovic 1972).

Decomposition of nitrous oxide has been described by a first-order rate expression (Johnston 1951; Laidler 1965):

$$-d[\text{N}_2\text{O}]/dt = k [\text{N}_2\text{O}] \quad (4)$$

Linders and Hinshelwood (1955a, b) have found that nitrous oxide decomposition kinetics deviate from first-order behavior, depending on the partial pressure of nitrous oxide and the presence of other gases. Rate coefficient data corresponding to Equation (4) that was given by Johnston (1951) is believed sufficient to estimate nitrous oxide decomposition rates in the gas phase, however:

$$k = 4.4 \times 10^{11} \exp[-60,000/RT] \quad (5)$$

where k has units of s^{-1} , R is the gas constant, 1.9872 cal/K-mol, and T is temperature (K). Equation (5) corresponds to data obtained in the temperature range 900 to 1050K, well above temperatures applicable to gas generation studies. Activation energies determined in other studies ranged from approximately 50 to 60 kcal/mole, with pre-exponential factors ranging from 10^{10} to nearly 10^{13} s^{-1} , as summarized by Preston and Cvetanovic (1972).

Clearly, the homogeneous unimolecular decomposition of nitrous oxide is unimportant at temperatures relevant to tank wastes. Following Equation (5) and approximately first-order rate behavior, more than 10^{18} years would be required for 1% of the nitrous oxide to decompose at 60°C. At 120°C, more than 10^{12} years would be required. Temperatures of 400°C or higher are predicted to be required to decompose 1% of the original nitrous oxide concentration within 1000 hours by this mechanism. Present data are consistent with this assessment, showing no measurable decomposition under thermal-only conditions.

Nitrous oxide decomposition reactions can be strongly affected by interactions with solids. These interactions result in lowering the activation energy for decomposition by approximately a factor of two. Compared with homogeneous gas phase reactions, Hinshelwood and Pritchard (1925a) determined an activation energy of 29.0 kcal/mole for the heterogeneous decomposition of nitrous oxide on a gold surface; the activation energy determined for this reaction was 32.5 kcal/mole for a platinum surface (Hinshelwood and Pritchard 1925b), 34.8 kcal/mole for a calcium oxide surface and 29.3 kcal/mole for an aluminum oxide surface (Schwab, Stager, and von Baumbach 1933).

A variety of metal oxide catalysts have been shown to be effective in catalyzing nitrous oxide decomposition as well. The effectiveness of oxide catalysts is as follows: $\text{Cu}_2\text{O} > \text{CoO} > \text{NiO} > \text{MgO} > \text{CaO} > \text{Al}_2\text{O}_3 > \text{ZnO} > \text{CdO} > \text{TiO}_2 > \text{Cr}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{Ga}_2\text{O}_3$ (Wagner and Hauffe 1938; Garner, Gray, and Stone 1950; Hauffe, Glang, and Engell 1950; Engell and Hauffe 1953; Dell, Stone, and Tiley 1953). Surface-catalyzed reactions have been proposed to follow this sequence (Wagner and Hauffe 1938):

where O^-_{ads} is a surface-adsorbed oxygen ion. Catalysts that are p-type (excess electron holes) are found to be the best catalysts for this reaction; catalysts that are n-type (excess electrons) are the poorest, while insulators are intermediate.

Heterogeneous reactions are expected to be of greatest relative importance at low temperatures (Laidler 1965). The velocity of a homogeneous unimolecular reaction is, according to absolute reaction rate theory,

$$v_{\text{hom}} = c_A [kT/h] [F_+/F_A] \exp[-E_{\text{hom}}/RT] \quad (9)$$

while that of a heterogeneous, surface-catalyzed reaction is

$$v_{\text{het}} = c_A c_S [kT/h] [1/F_A] \exp[-E_{\text{het}}/RT] \quad (10)$$

where c_A and c_S are concentrations of nitrous oxide in the gas phase and on a solid surface, respectively, E_{hom} and E_{het} are activation energies for homogeneous and heterogeneous reactions, respectively, and F_+ and F_A are partition functions for the activated complex and for nitrous oxide in the gas phase, respectively. Dividing Equation (10) by Equation (9), one obtains

$$v_{\text{het}}/v_{\text{hom}} = c_S/F_+ \exp[\Delta E/RT] \quad (11)$$

where ΔE is $E_{\text{hom}} - E_{\text{het}}$. For 1 cm^2 of solid surface area, the term c_S is approximately 10^{15} , whereas for 1 cm^3 of nitrous oxide gas, F_+ is approximately 10^{27} . Following the above discussion, ΔE is approximately 30 kcal/mole for nitrous oxide reactions. Thus we have

$$v_{\text{het}}/v_{\text{hom}} \approx 10^{-12} \exp[30,000/RT] \quad (12)$$

From Equation (12), which is based on absolute rate theory, heterogeneous reactions are predicted to dominate for temperatures less than approximately 300°C. Of course, actual reaction rates may vary widely, depending on the catalytic properties of the solid surface. It can be concluded that any experimental observation of nitrous oxide decomposition at temperatures relevant to waste storage must be due to surface-mediated reactions, not to true gas-phase reactions.

Nitrous oxide decomposition in glass reaction vessels has been attributed to catalysis by the glass walls in studies conducted by Ashby et al. (1994b). Nitrous oxide decomposition catalyzed by glass surfaces has long been recognized (Hibben 1928; Lindars and Hinshelwood 1955a). Experiments of Ashby et al. (1994b) were conducted at 120°C in glass reaction vessels for approximately 1000 hours. The first-order rate constant determined was approximately 10^{-7} s^{-1} , whether simulated waste mixtures were present in the reaction vessel or not. This rate constant is many orders of magnitude larger than expected from Equation (5). Ashby et al. (1994b) noted that the above rate constant has meaning only for a particular apparatus that was used, because the value depends on the glass surface-area-to-gas-volume ratio. Rates may also be expected to vary with the surface composition of the glass vessel, which may change with age and use.

That stainless steel used in the present studies would have little influence on nitrous oxide decomposition rates is not unexpected. The surface of the stainless steel is expected to be high in chromium oxide and iron oxide (Baer and Dake 1986; Briant and Mulford 1982). Oxides of iron and chromium are known to be poor catalysts for this reaction (Wagner and Hauffe 1938; Garner, Gray, and Stone 1950; Hauffe, Glang, and Engell 1950; Engell and Hauffe 1953; Dell, Stone, and Tiley 1953). In contrast, Ashby et al. (1994b) did find that nitrous oxide was thermally decomposed in glass vessels under otherwise similar conditions. While the type of glass used was not identified, compositions typically used in laboratory glassware include silica, alumina, boron oxide, sodium oxide, calcium oxide, magnesium oxide, and other components (Doremus 1973). As discussed above, aluminum oxide and the alkaline earth oxides have been found to be more effective catalysts for nitrous oxide decomposition than are the oxides of iron or chromium.

In the Hanford waste tanks, the steel walls are expected to contribute negligibly to nitrous oxide decompositions. Not only is the expected catalytic activity of the steel for this reaction quite low, but the tank surface-area-to-volume ratio is very small. Gases trapped as bubbles in the sludge will not contact the steel tank walls. Once released to the plenum space above the wastes, the gases will be removed through the ventilation system in a relatively short time.

Catalysis of nitrous oxide decomposition by solid phases present in the waste is a significant possibility, however. Gases are believed to be retained in the nonconvective layer of some of these waste tanks as gas bubbles attached to solid particles, in response to surface tension forces (Bryan, Pederson, and Scheele 1992). Thus the gases will be in intimate contact with tank solids, which include sodium aluminate, sodium nitrate, sodium nitrite, sodium carbonate, and other phases (Herting et al. 1992a, b). From results of the present study, the possible catalysis of nitrous oxide decomposition by such solids cannot be assessed, because simulant mixtures were excluded from the tests. Ashby et al. (1994b) found no difference in nitrous oxide decomposition rates whether simulants were present or absent. However, those experiments may have been dominated by catalysis by their glass reaction vessels. The influence of tank solids on gaseous decomposition kinetics remains to be assessed.

3.1.3 Radiolytic Decomposition of Nitrous Oxide

The radiation chemistry of nitrous oxide is complex, and the complete mechanism of reaction has not been fully developed (Spinks and Woods 1990). Nitrous oxide finds use as a gas-phase dosimeter (Johnson 1973) and as an electron scavenger (Harteck and Dondes 1956). Products of radiolytic reactions of nitrous oxide include nitrogen, oxygen, and nitric oxide. G-values for these products are 1.04 ± 0.02 , 0.41 ± 0.04 , and 0.41 ± 0.04 $\mu\text{moles/J}$, respectively, or 10.0, 3.9, and 3.9 molecules/100 eV, respectively (Spinks and Woods 1990).

Radiolytic yields obtained in this study for nitrous oxide decomposition, corresponding to relatively low total doses, are in excellent agreement with literature values (Harteck and Dondes 1956; Simpson 1961), as given in Table 2. Literature values and present results were in agreement despite present measurements being made in the temperature range of 60 to 150°C, while literature results were obtained at 25°C. This finding emphasizes the lack of a temperature dependence for radiolytic reactions of nitrous oxide. At higher radiation doses ($\approx 1.7 \times 10^8$ R), measured G-values deviated substantially from literature values. Harteck and Dondes (1956) noted that G-values for nitrous oxide decomposition were not constant above total doses of 10^9 R, due to secondary reactions of the initial products.

Nitric oxide will react instantly with oxygen to form nitrogen dioxide, following Cotton and Wilkinson (1980):

If water vapor is present, nitrogen dioxide will react with water to yield nitric acid and nitric oxide, a reaction that is used widely on an industrial scale. Another reaction of potential importance in the waste tanks is the reaction of nitrogen dioxide, water vapor, and ammonia to yield ammonium nitrate (Bou-Hamra 1988; Pederson and Bryan 1994), which also is used on an industrial scale. In Tank 241-SY-101, however, which is closely monitored by infrared spectrometry and other probes, neither nitrogen dioxide nor nitric oxide been observed, nor have ammonium nitrate solids been detected (see Pederson and Bryan 1994 and references therein).

Thermodynamically unstable, nitric oxide will decompose to yield nitrous oxide and nitrogen dioxide, following Cotton and Wilkinson (1980):

Equation (14) is important only for high nitric oxide pressures where collisions between NO molecules are more probable (Melia 1965), and should be of little importance in Hanford Site waste tanks.

Among gases likely to be formed in the Hanford Site waste tanks, nitrous oxide is unique in its ability to capture electrons, following (Spinks and Woods 1990):

Oxygen ions can then react further with nitrous oxide molecules:

The ionic species NO^- will decompose to yield NO and an electron, which can then react following Equation (15). In aqueous systems, nitrous oxide is effective in scavenging hydrated electrons to yield hydroxyl radicals and nitrogen gas. However, this reaction is overshadowed by hydrated electron scavenging by the nitrate ion in Hanford Site tank wastes (Meisel et al. 1993).

The extent of nitrous oxide decomposition due to gas phase radiolytic reactions is readily estimated. Assuming a gamma dose rate in the wastes of $\approx 10^3$ R/h, a value of $G(\text{-N}_2\text{O})$ of -12 molecules/100 eV (Harteck and Dondes 1956), and a gas mixture composed of 30% nitrous oxide, 30% nitrogen, 30% hydrogen, and 10% ammonia, it is estimated that 0.9% of the nitrous oxide will be decomposed each year. Thus the impact of nitrous oxide radiolysis in the gas phase on gas product distributions is expected to be relatively minor. Radiolysis coupled with catalytically active solids surfaces may be important and should be considered further, however.

3.2 Reactions of Nitrous Oxide and Hydrogen

Nitrous oxide and hydrogen are two of the principal gases produced by thermal and radiolytic reactions in Tank 241-SY-101, each accounting for approximately 30 mole percent of the total (LANL 1994). Nitrous oxide and hydrogen are known to react to produce ammonia, nitrogen, oxygen, and water, depending on conditions. Experimental results on thermal and combined thermal and radiolytic reactions of nitrous oxide and hydrogen reactions are described in Section 3.2.1. In Section 3.2.2, thermally driven reactions of nitrous oxide are discussed, including a survey of the literature and comparison to present results. Section 3.2.3 addresses nitrous oxide and hydrogen reactions under combined radiolytic and thermal conditions.

3.2.1 Experimental Results for Nitrous Oxide and Hydrogen Reactions

Reactions of nitrous oxide and hydrogen were probed under thermal and combined thermal and radiolytic conditions in ≈ 500 -mL stainless steel vessels. Reaction times extended to ≈ 500 hours, reaction temperatures were 60, 90, and 120°C , and radiation dose rates were 0, 1.5×10^2 , and 1.7×10^4 R/h. Initial concentrations of N_2O and H_2 gases were intentionally kept at or below approximately 2 mole percent to ensure that the mixture did not exceed the lower flammability limit. An inert gas (argon) was added as a diluent at an approximate concentration of 96 mole percent for that purpose.

Gas analyses were performed using mass spectrometry and infrared spectrometry. Mass spectrometry results for ammonia and water vapor are not considered to be quantitative; these gases are well known to adsorb onto the walls of the apparatus, resulting in an underestimate of their concentrations. Ammonia concentrations were obtained using a Fourier transform-infrared spectrometer (FTIR) that was equipped with a gas cell. For ammonia analysis, the 967 wavenumber band was used. Water concentrations were not able to be measured quantitatively, due to the use of KBr optics in the FTIR gas cell. Even though water is certainly formed, our analyses are not considered to be reliable so they

were not reported. Calibration of the FTIR/gas cell was accomplished using a calibrated gas leak tube. Infrared spectrometry also provides concentration data for nitrous oxide but is not sensitive to molecules having no permanent dipole moment, such as hydrogen, nitrogen, and oxygen.

Under thermal-only conditions, the principal products of nitrous oxide reactions with hydrogen were nitrogen, oxygen, water, and a very small concentration of ammonia. Under combined thermal and radiolytic conditions, while similar products were found as for thermal-only conditions, the extent of nitrous oxide and hydrogen consumption and of ammonia formation was considerably greater. Gas compositions before and after reactions under thermal and combined thermal and radiolytic conditions are given in Table 3. Infrared spectra corresponding to thermal reactions and thermal/radiolytic reactions are given in Figures 7 through 9. The highest radiation doses corresponded to the greatest quantity of ammonia, nitrogen, oxygen, and water produced, with a concomitant decrease in the concentrations of nitrous oxide and hydrogen.

Radiolytic yields and reactant consumption for the reaction of hydrogen and nitrous oxide showed a strong dependence on total radiation dose. G-values for nitrous oxide and hydrogen disappearance and for nitrogen, oxygen, water, and ammonia formation are given in Table 4, calculated from the results given in Table 3. Tests carried out at the low total dose (about $7 \times 10^6 \text{R}$) gave higher radiolytic product yields than those performed at high dose (about $2 \times 10^8 \text{R}$). Nitrous oxide and hydrogen were more than 90% consumed in the high dose experiments, whereas only approximately 20% of the reactants were consumed in the low dose tests. For that reason, G-values corresponding to the low dose tests are considered to be more reliable.

Consumption of nitrous oxide and hydrogen was dependent on temperature for the low radiation dose tests (about $7 \times 10^6 \text{R}$). The smallest values for $G(-\text{N}_2\text{O})$ and $G(-\text{H}_2)$ were obtained at 60°C . This behavior contrasts with results described in Section 3.1, where it was shown that the radiolytic decomposition of nitrous oxide to nitrogen and oxygen was essentially independent of temperature. The absolute value of $G(-\text{N}_2\text{O})$ in the presence of hydrogen is approximately double that determined when hydrogen was absent (see Tables 2 and 4). The observation that $G(-\text{N}_2\text{O})$ and $G(-\text{H}_2)$ are essentially identical for each experiment indicates that an added pathway for nitrous oxide decomposition exists beyond the mechanisms discussed in Section 3.1.

In addition to increased consumption of nitrous oxide and hydrogen with increased temperature, for a constant radiation dose, ammonia yields also increased. Ammonia yields are included in Table 4. As more ammonia was produced, a concomitant decrease in molecular nitrogen production was observed. At 60°C , nitrogen yields nearly matched the nitrous oxide consumption. Nitrogen accounted for only one-third to one-half of the quantity of nitrous oxide consumed at 90 and 120°C , however. This coincides with increased ammonia production.

The poorest mass balance was encountered for the highest total doses. Mass balance may have suffered because some of the products were not fully in the gas phase. For example, with water formation, ammonia and nitrogen dioxide could equilibrate with an adsorbed layer and not be readily detected.

Table 3. Gas Phase Composition of Nitrous Oxide and Hydrogen Reactions Under Thermal and Radiolytic Conditions

	gas composition, mol%						conditions	dose
	<u>N₂O</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>NH₃</u>	<u>Ar</u>		
initial	3.52	3.42	0.0087	0	0	93.04	60°C	0
terminal	3.22	3.21	0.042	0.0008	0.0033	93.54		
initial	3.52	3.42	0.0087	0	0	93.04	60°C	7.2 x 10 ⁶ R
terminal	2.94	3.01	0.55	0.058	0.0098	93.4		
initial	3.58	3.4	0.279	0.057	0	92.7	60°C	1.83 x 10 ⁸ R
terminal	0.147	0.031	3.26	0.006	0.026	96.5		
initial	3.58	3.4	0.279	0.057	0	92.7	90°C	0
terminal	3.37	3.32	0.082	0.0039	0.042	93.2		
initial	2.91	2.92	0.009	0	0	94.1	90°C	7.7 x 10 ⁶ R
terminal	1.82	1.81	0.41	0.028	0.022	95.9		
initial	2.91	2.92	0.009	0	0	94.1	120°C	0
terminal	2.7	2.76	0.169	0.039	0.22	94.33		
initial	3.15	3.1	0.0	0.0	0	93.7	120°C	7.4 x 10 ⁶ R
terminal	2.32	2.27	0.395	0.004	0.022	95.0		
initial	2.91	2.92	0.009	0	0	94.1	120°C	1.68 x 10 ⁸ R
terminal	0.113	0.26	2.16	0.008	0.0089	97.4		
initial	2.91	2.92	0.009	0	0	94.1	150°C	0
terminal	2.42	2.76	0.451	0.029	0.29	94.34		
initial	3.15	3.1	0.0	0.0	0	93.7	150°C	7.4 x 10 ⁶ R
terminal	2.06	2.07	0.53	0.005	0.0007	95.3

Figure 7. Thermal and Radiolytic Reaction of Nitrous Oxide and Hydrogen (initial mixture contained 1 mol% N₂O and 1 mol% H₂ in argon; 300 hours reaction time at 90°C)

Figure 8. Infrared Spectrum Detailing Ammonia Region for Thermal and Radiolytic Reaction of Nitrous Oxide and Hydrogen

Table 4. G-Value Measurements for the Reaction of Nitrous Oxide and Hydrogen

G Value (molecule/100 eV)					conditions	dose (R)
<u>G(N₂O)</u>	<u>G(H₂)</u>	<u>G(N₂)</u>	<u>G(O₂)</u>	<u>G(NH₃)</u>		
-21.8	-15.7	19.3	2.06	0.35	60°C	7.2 × 10 ⁶ R
-4.8	-4.7	4.1	0	0.36	60°C	1.83 × 10 ⁸ R
-36.2	-36.8	13.2	0.92	0.73	90°C	7.7 × 10 ⁶ R
-29.1	-29.1	13.6	0.14	0.76	120°C	7.4 × 10 ⁶ R
-4.3	-4.1	3.3	0.01	0.014	120°C	1.65 × 10 ⁸ R
-38.0	-35.9	18.3	0.18	0.024	150°C	7.4 × 10 ⁶ R

3.2.2 Thermally Driven Reactions of Nitrous Oxide and Hydrogen: Literature Review and Discussion

Compared with other oxides of nitrogen, nitrous oxide is considered to be relatively unreactive (Samsonov 1973; Jones 1975; Cotton and Wilkinson 1980). Nitrous oxide will react with hydrogen following

Hydrogen/nitrous oxide reactions are more exothermic than analogous reactions of hydrogen in air or oxygen because nitrous oxide has a higher free energy (and heat) of formation than molecular oxygen. Autoignition temperatures are also lower for nitrous oxide/hydrogen mixtures than for corresponding mixtures of hydrogen with oxygen or air. Explosion limits for nitrous oxide and hydrogen mixtures are extremely wide (Jones 1975). The apparent downward lean limit is 6% for hydrogen in nitrous oxide for spark ignition compared with 8% for H₂ in air (Hertzberg and Zlochower 1994). The true limit appears to be much lower. Using a pyrotechnic initiator of 1000 J, the apparent limit is approximately 2% hydrogen in nitrous oxide. Even smaller values were reported using more energetic pyrotechnic initiators (Hertzberg and Zlochower 1994). Nitrous oxide and hydrogen mixtures diluted with up to 79% nitrogen may still be explosive (Jones 1975).

Rates of reaction of hydrogen and nitrous oxide are not dependent simply on the rate of dissociation of nitrous oxide but on the concentrations of both nitrous oxide and hydrogen. Melville (1934) suggested the following scheme:

The symbol * in the reactions given above indicates a molecule activated through collisions.

Nitrous oxide and hydrogen reactions may be catalyzed by solid surfaces. Reaction following Equation (17) on gold surfaces is of a very unusual type (Hutchinson and Hinshelwood 1926; Laidler 1965). This reaction is an example of noncompetitive adsorption, where the two molecules adsorb on different surface sites without displacing each other from the metal surface. Rates of reaction are very different from the more common case of a gas molecule interacting with an adsorbed molecule. No literature has been found describing nitrous oxide and hydrogen reactions catalyzed by materials other than gold. As described in Section 3.1.2, however, nitrous oxide reactions are most effectively catalyzed by p-type metal oxides, whereas hydrogen reactions are most effectively catalyzed by metals and n-type metal oxides (Laidler 1965). Preferential adsorption sites on a solid surface for the two gases are thus likely to be quite different in character.

Nitrous oxide consumption under thermal-only conditions was greater in the presence of hydrogen than in its absence (compare Tables 2 and 4), consistent with earlier findings that nitrous oxide/hydrogen reaction rates depend on the concentration of both gases (Melville 1934; Laidler 1965). The consumption of nitrous oxide was always slightly greater than that of hydrogen, however, which is not expected if the overall reaction is described by Equation (17). A summary of rate-constant calculations is provided in Table 5 for this second-order reaction. From the work of Hertzberg and Zlochower (1994), it is apparent that even very small additions of hydrogen to nitrous oxide are effective in catalyzing decomposition reactions, which can occur explosively when initiated with a spark or pyrotechnic device. If hydrogen serves as a catalyst, it is not surprising that the stoichiometry of the reaction deviates from Equation (17).

Table 5. Rate Data for Nitrous Oxide/Hydrogen Reactions Under Thermal-Only Conditions

Temperature	N ₂ O Composition (%)	H ₂ Composition (%)	Rate Constant Based on N ₂ O Composition L/mol-s	Rate Constant Based on H ₂ Composition L/mol-s
60	9.1	6.7	4.8e-5	3.5e-5
90	6.4	2.9	3.4e-5	1.4e-5
120	7.6	5.8	5.3e-5	4.1e-5

Rate constants given in Table 5 show no clear dependence on temperature, contrary to what might be expected for bimolecular gas phase reactions (Melville 1934). With an activation energy of 40 kcal/mole, the bimolecular reaction should proceed approximately 10^4 times faster at 120°C than at

60°C, which obviously is not the case. Catalysis by the stainless steel vessel surfaces may be the controlling feature, although no literature was found that would confirm this assertion. Catalyzed reactions are usually characterized by a significantly lower activation energy (Thomas and Thomas 1969). An inverse relation between the concentration of surface-adsorbed species and temperature also will diminish the temperature dependence of catalyzed reaction rates. Regardless of the mechanism, the extent of nitrous oxide/hydrogen reactions under thermal conditions would appear to be sufficiently large to affect gas product ratios in both actual wastes and in laboratory tests with simulated wastes.

In addition to the formation of water and nitrogen in the present experiments following Equation (17), ammonia was also a product. Ammonia formation under combined thermal and radiolytic conditions was more extensive than under thermal-only conditions, as described in Section 3.2.1. No literature was found that describes the direct conversion of nitrous oxide and hydrogen to ammonia under thermal or under combined thermal and radiolytic conditions. Nitrogen is a decomposition product of nitrous oxide, however, as described above. The reactions of nitrogen and hydrogen to yield ammonia have been studied and are described in Section 3.3.

Another potential product of the reaction of nitrous oxide and hydrogen is hydrazine (N_2H_4). Used as a rocket fuel, hydrazine will burn in air accompanied with a considerable evolution of heat (149 kcal/mole) (Cotton and Wilkinson 1980). Hydrazine is also considered to be quite toxic (Sax 1979). In basic solutions, hydrazine is a strong reducing agent. Reactions that are known to produce hydrazine and involve nitrous oxide, hydrogen, or the reaction products nitrogen, oxygen, and/or ammonia are

Reactions (25) through (27) are considered to be of minor importance (Cotton and Wilkinson 1980). Rather, Reactions (28) through (30) are thermodynamically favored due to the strength of the $N \equiv N$ bond:

No hydrazine was observed by infrared spectrometry, under either thermal-only or combined thermal and radiolytic conditions (see Figure 9, which includes a spectra for gas products and a standard spectra for hydrazine obtained from the Nicolet spectral database^(a)). Principal spectral features for hydrazine overlap substantially with those for ammonia, which would limit detection of small quantities of hydrazine in this matrix. Hydrazine is highly soluble in water; any residual water that might be

(a) The database is maintained by Nicolet Analytical Instrument Corporation.

present could scavenge this compound. In addition, the boiling point of hydrazine is 113°C. At room temperature (at which infrared analyses are performed), a substantial fraction would be present as the liquid. It is possible that hydrazine be present without detection by gas phase FTIR analysis.

3.2.3 Combined Thermal and Radiolytic Reactions of Nitrous Oxide and Hydrogen

The addition of hydrogen to nitrous oxide has been reported to have little impact on the extent of radiolytic decomposition of nitrous oxide or on the formation of nitrogen (Hearne and Hummel 1961). Yields of oxygen and nitrogen oxides are reported to be less with hydrogen present, however (Hearne and Hummel 1961). After absorbing energy from impinging radiation, excited nitrous oxide molecules can decompose following (Anderson 1968):

Further reactions of the O and N atoms with nitrous oxide can occur:

Hydrogen molecules can react with atomic oxygen:

which would suppress both Reactions (34) and (35), thereby lowering both oxygen and nitric oxide yields. Hydrogen atoms may also react with nitrous oxide molecules to form molecular nitrogen and hydroxyl radicals (Hearne and Hummel 1961):

In the present study, quantities of nitrous oxide consumed in combined radiolytic and thermal reactions were substantially increased by the presence of hydrogen. As given in Table 4, for a given radiation dose, the absolute value of $G(-\text{N}_2\text{O})$ in the presence of hydrogen was more than double that obtained without the inclusion of hydrogen in the reaction mixture. The rate-determining step in the thermal and radiolytic reaction of hydrogen and nitrous oxide cannot simply be the unimolecular decomposition of nitrous oxide. Processes such as Reaction (37) must also be important.

The extent of consumption of nitrous oxide in Tank 241-SY-101 via reaction with hydrogen may be estimated from the G-values given in Table 4. Assuming a dose rate of 1000 R/h, a gas composed approximately of 30 mole percent nitrogen, 30 mole percent nitrous oxide, 30 mole percent hydrogen, and 10 percent ammonia, a value of $G(-\text{N}_2\text{O})$ of 30 molecules/100 eV, and assuming that all the absorbed energy is channeled into nitrous oxide/hydrogen reactions, approximately 2.2% of the nitrous

oxide will be consumed per year. Although greater than the quantity consumed by the unimolecular decomposition of nitrous oxide (0.9%), reactions of nitrous oxide and hydrogen by combined radiolytic and thermal reactions would still not appear to be sufficiently high to measurably alter gas product distributions in the Hanford Site waste tanks. The extent of reaction may be enhanced via catalysis by tank solids, however; this aspect has not yet been addressed.

Figure 9. (A) Radiolytic and Thermal Reaction Products from Mixture of 1.9% H_2 and 1.7% N_2O (2×10^4 R/h, 90°C , 400 hours; (B) Database Spectrum of Hydrazine (N_2H_4).

3.3 Reactions of Nitrogen and Hydrogen

Nitrogen and hydrogen are two of the principal gases produced by thermal and radiolytic reactions in Tank 241-SY-101, each accounting for approximately 30 mole percent of the total (LANL 1994). Nitrogen and hydrogen are known to react to produce ammonia under thermal and radiolytic conditions. Experimental results on thermal and on combined thermal and radiolytic reactions of nitrogen and hydrogen are described in Section 3.3.1. In Section 3.3.2, thermally driven reactions of nitrogen and hydrogen are discussed. Section 3.3.3 addresses nitrogen and hydrogen reactions under combined thermal and radiolytic conditions.

3.3.1 Experimental Results for Reactions of Nitrogen and Hydrogen

Reactions of nitrogen and hydrogen were assessed under both thermal-only and combined thermal and radiolytic conditions. Reactions were performed in stainless steel vessels having a ≈ 500 -mL capacity. Reaction times extended to approximately 700 hours, the reaction temperature was 90°C , and radiation dose ranged from 0 to 1×10^7 R. The reactants N_2 and H_2 were initially mixed in a 20:1 mole ratio and injected into each reaction vessel initially purged with argon. Gas analyses were performed after the experiment by mass spectrometry and infrared spectroscopy. Mass spectrometry provided information on the concentrations of nitrogen, hydrogen and argon, while infrared spectrometry provided a means to determine ammonia concentrations. Table 6 contains the concentrations of gases at the termination of reaction. Because the conversion of nitrogen and hydrogen to products was extremely small, the concentrations for nitrogen, hydrogen, and argon were assumed to be constant throughout the experiment for purposes of calculating G values. Figure 10 shows infrared spectra of the products of the nonradiolytic and radiolytic reaction of nitrogen and hydrogen. Ammonia is readily apparent as a radiolytic reaction product.

Ammonia was formed from the reaction of nitrogen and hydrogen under both thermal-only and combined thermal and radiolytic conditions. Thermal yields were near the detection limit by infrared spectrometry. Ammonia yields increased with increased total radiation dose. It was not possible to assess any dose rate dependence from these tests.

An inverse relation between total dose and $G(\text{NH}_3)$ was found in this study. Values for $G(\text{NH}_3)$ are given in Table 7 and Figure 11 as a function of total radiation dose. Radiolytic ammonia yields fell from a high of nearly one molecule per 100 eV absorbed radiation for a total dose of 5.9×10^4 R/h to a low of approximately 0.01 molecules per 100 eV for a total dose of 1.1×10^7 R/h. This behavior may be ascribed to competing ammonia formation and decomposition reactions, leading to essentially a steady state ammonia concentration. Values of $G(\text{NH}_3)$ corresponding to the lowest radiation doses are thus expected to be most reliable.

Figure 10. Infrared Spectra of Thermal and Radiolytic Reaction Products of Hydrogen and Nitrogen (initial mixture contained 20:1 mole ratio of N₂:H₂; temperature 90°C; 4 weeks)

Table 6. Composition of Reactant Gas Mixture and Products for Radiolytic Reaction of Nitrogen and Hydrogen

mol %			moles produced	dose (R)
<u>N₂</u>	<u>H₂</u>	<u>Ar</u>	<u>NH₃</u>	
13.3	0.75	85.9	1.02E-07	1.1 x 10 ⁷ R
84.5	4.57	10.8	1.36E-06	6.8 x 10 ⁶ R
9.4	0.53	90	8.91E-08	4.2 x 10 ⁵ R
54.9	2.9	42.2	8.30E-08	2.5 x 10 ⁵ R
9.9	0.56	89.5	5.63E-08	9.6 x 10 ⁴ R
39.1	2	58.9	4.10E-08	5.9 x 10 ⁴ R

Table 7. G-Value Measurements for the Reaction of Nitrogen and Hydrogen

G Value (molecules/ 100 eV)	<u>conditions</u>	<u>dose</u>
<u>G(NH₃)</u>		
0.0099	90°C	1.1 x 10 ⁷ R
0.15	90°C	6.8 x 10 ⁶ R
0.25	90°C	4.2 x 10 ⁵ R
0.45	90°C	2.5 x 10 ⁵ R
0.74	90°C	9.6 x 10 ⁴ R
0.89	90°C	5.9 x 10 ⁴ R

Figure 11. G-Values For Ammonia Production from Nitrogen and Hydrogen

3.3.2 Thermally Driven Reactions of Nitrogen and Hydrogen

The Haber process is used on an industrial scale to produce ammonia from the reaction of hydrogen and nitrogen in the presence of a catalyst (Thomas and Thomas 1969; Bottomley and Burns 1979). The reaction

is exothermic and is thermodynamically favored by low temperatures and high pressures. However, because of kinetic considerations, industrial ammonia synthesis is performed typically in the temperature range of 400 to 550°C and 100 to 1000 atmospheres total pressure.

The use of catalysts in ammonia synthesis following Reaction (38) is essential (Thomas and Thomas 1969; Bottomley and Burns 1979; Cotton and Wilkinson 1980). Industrial catalysts commonly consist of reduced oxides of iron promoted with metal oxides such as alumina, silica, or zirconia. Alkali and alkaline earth promoters have also been used. The rate-determining step in ammonia synthesis from nitrogen and hydrogen is the dissociative adsorption of nitrogen onto those catalyst surfaces. In the absence of an appropriate catalyst and at temperatures relevant to Hanford Site waste tanks, the expected rate of ammonia formation from the thermally driven reaction of nitrogen and

hydrogen is infinitesimally small. The observation of a small yield of ammonia in the present experiments performed at 90°C without radiation present almost certainly can be attributed to catalysis by the stainless steel reaction vessel.

3.3.3 Combined Radiolytic and Thermal Reactions of Nitrogen and Hydrogen

The synthesis of ammonia from its elements and the decomposition of ammonia by radiolytic processes have been studied extensively (Spinks and Woods 1990). Ammonia can be produced from the gas-phase reaction of hydrogen and nitrogen in the presence of gamma radiation. Ammonia yields are usually quite low, with $G(\text{NH}_3)$ ranging from ≈ 0.7 to 1.5 molecules/100 eV (Spinks and Woods 1990). For a gas mixture containing 30% nitrogen and 70% hydrogen at a total pressure of approximately 50 atm and at 25°C, $G(\text{NH}_3)$ has been given as 0.98 molecules/100 eV (CRC 1986). Results for $G(\text{NH}_3)$ corresponding to low total doses in this study are in good agreement with literature values.

The rapidly falling radiolytic yield of ammonia with increased dose shown in Figure 11 emphasizes the fact that ammonia can not only be synthesized by radiolytic processes but also decomposed. Ammonia decomposition reactions are discussed in more detail in Section 3.3.4. A number of reaction pathways yield ammonia, both thermal and radiolytic, in the Hanford Site tank wastes. These have been addressed by Ashby et al. (1994b) and Meisel et al. (1993). Gas phase reactions of nitrogen and hydrogen by thermal and combined thermal and radiolytic processes ranks as only a very minor source of ammonia, compared to solution phase reactions involving the nitrite ion and organic waste components. Radiolytic gas phase reactions may serve to limit the maximum concentration of ammonia that is possible rather than contribute substantially to the quantity produced.

3.4 Ammonia Decomposition Reactions

3.4.1 Thermal Decomposition of Ammonia

As in the case of nitrous oxide decomposition reactions, ammonia decomposition via a homogeneous, unimolecular mechanism is important only at high temperatures. High temperatures are required because the $\text{NH}_2\text{-H}$ bond dissociation energy is nearly 100 kcal/mole (Homann and Haas 1972). The heterogeneous decomposition catalyzed by solid surfaces is much more probable at temperatures relevant to Hanford Site tank wastes.

An expression for the rate constant for homogeneous ammonia decomposition has been given by Michel and Wagner (1965) for the temperature range of 2100K to 2900K:

$$k_{\text{hom}} = 4.4 \times 10^{12} \exp[-79.5 (\pm 2.5)/RT] \text{ l/mole-s} \quad (39)$$

This second-order rate constant was first-order with respect to ammonia and first-order with respect to the diluent argon. A similar expression has been given by Jacobs (1963) but with an activation energy of 77.7 kcal/mole and a pre-exponential factor of 2.5×10^{13} l/mole-s. Jacobs (1963) determined, based on shock tube experiments, that the reaction order with respect to ammonia was 3/2, while the order with respect to argon was 1/2. Regardless of which (if either) expression is correct, the extent of ammonia decomposition expected at tank temperatures by homogeneous unimolecular decomposition is infinitesimally small and may be neglected.

Substantially lower activation energies have been reported for ammonia decomposition reactions catalyzed by metal surfaces. Activation energies of 38 kcal/mole have been reported for tungsten surfaces (Hinshelwood and Burke 1925), 38 to 43 kcal/mole for molybdenum surfaces (Kunsman 1928) and 48 kcal/mole for osmium surfaces (Arnold and Burk 1932). From Equation (11), derived from absolute rate theory, and using a value of $\Delta E \approx 40$ kcal/mole, it is estimated that heterogeneous reactions should dominate for temperatures less than approximately 450°C. Of course, that estimate will change substantially, depending on the catalytic activity of the solid surface. The extent of decomposition of ammonia by either homogeneous or heterogeneous pathways at tank temperatures is expected to be extremely small, however (Homann and Haas 1972).

3.4.2 Radiolytic Decomposition of Ammonia

Ammonia is decomposed under radiolytic conditions. Depending on the temperature, dose rate, and ammonia partial pressure, products include nitrogen, hydrogen, and hydrazine. Radiolytic reactions involving ammonia have been reviewed by Spinks and Woods (1990), from which much of the following discussion has been taken.

Unlike nitrous oxide decomposition reactions under radiolytic conditions, which are largely temperature-independent at moderate temperatures, G-values for ammonia decomposition are temperature-dependent. The value for $G(-NH_3)$ increases from 0.35 $\mu\text{mol/J}$ at 20°C to a plateau of approximately 1 $\mu\text{mol/J}$ at 150°C for an ammonia partial pressure of 1 atm. The value for $G(-NH_3)$ also depends on the ammonia partial pressure, falling from a value of 0.40 $\mu\text{mol/J}$ at 0.1 atm to 0.35 $\mu\text{mol/J}$ at 1 atm at 20°C. At 120°C, $G(-NH_3)$ falls from 1 $\mu\text{mol/J}$ at 1 atm to 0.68 $\mu\text{mol/J}$ at 60 atm. These trends emphasize the finding that ammonia decomposition reactions are quite complex and involve multiple steps.

From $G(-NH_3)$ values obtained from the literature, the extent of radiolytic decomposition of ammonia in the gas phase in Hanford Site waste tanks may be estimated. As before, a gamma dose rate of 1000 R/h is assumed. A $G(-NH_3)$ value of 6.3 molecules/100 eV is estimated from the work of Sorokin and Pshezhetskii (1964), corresponding to a temperature of 60°C and an ammonia partial pressure of 0.2 atm. In one year, it is readily calculated that 0.15% of the ammonia initially present in the wastes will be decomposed to nitrogen and hydrogen. Such losses will be more than offset by the production of ammonia via complexant degradation reactions (Ashby et al. 1994b; Meisel et al. 1993; Bryan and Pederson 1994).

4.0 Comparison of Gas Generation Rates in Supernate and Solid Fractions of Tank 241-SY-101 Simulated Waste

Bryan and Pederson (1994) obtained gas generation rates from a homogeneous simulated waste, SY1-SIM-93B, that were approximately a factor of ten smaller than those obtained for a simulated waste slurry, SY1-SIM-91A. Both simulants contained the principal inorganic components of actual tank wastes, although in different concentrations; these were sodium aluminate, sodium nitrite, sodium nitrate, sodium carbonate, and sodium hydroxide. The two simulants contained identical concentrations of trisodium HEDTA, the only organic component. Differences in rates of gas generation could not be readily explained by differences in concentrations of key components, suggesting that inorganic solid surfaces may have enhanced reactions leading to flammable gas production. In this study, the heterogeneous simulant SY1-SIM-92A containing trisodium HEDTA as the sole organic constituent was separated into two fractions, settled solids and supernatant liquid. In addition to the principal inorganic components, this simulant also contains transition metal nitrates and other minor components known to be present in actual wastes (Bryan and Pederson 1994). Gas generation rates were then determined for the two fractions to more directly assess the possible catalytic role of inorganic solid surfaces.

4.1 Preparation and Characterization of Simulant Fractions

The simulant SY1-SIM-92A was prepared as described by Bryan and Pederson (1994). The composition of this simulant is given in Table 8. The organic carbon content was 1.57 weight percent (wt%), added as trisodium HEDTA. After the batch was prepared, the mixture was equilibrated by stirring continuously for approximately 24 hours at 25°C. The simulant mixture was then centrifuged at approximately 2400g (3300 rpm, 40-cm-diameter centrifuge) for one hour at 25°C. Following centrifugation, the supernatant liquid was separated from the settled solids by decanting. The supernatant liquid composed 68.5 wt% of the total mass of the original simulant; the settled solids composed the remaining 31.5 wt%. The densities of the supernate and centrifuged solids phases were 1.52 g/mL and 1.63 g/mL respectively.

The water content of the supernatant liquid and settled solids fractions was determined by weight loss following heating to 225°C in a Perkin-Elmer Model TGA-7 Thermogravimetric Analyzer (TGA). Information on both free water and waters of hydration are obtained by this procedure. No attempt was made to distinguish between the forms of water, however. The water content of the supernatant liquid and settled solids was 48 ± 3 and 29 ± 2 wt%, respectively.

The total organic carbon (TOC) content of both fractions was also determined. The TOC was determined using the hot persulfate oxidation/coulometry detector method, Test Procedure PNL-ALO-381 Rev.0, "Determination of TC, TOC, and TIC in Radioactive Liquids, Soils, and Sludges by Hot Persulfate Method." This is a two-step procedure in which total inorganic carbon is obtained by hot acid decomposition of the carbonate, TOC is then obtained by silver-catalyzed oxidation of the same sample, and total carbon is calculated by addition. Runs were made in duplicate. The given error represents the range of values obtained (e.g., high - low /2). The average value was reported. The supernatant liquid was found to contain 2.2 ± 0.2 wt% TOC, while the settled solids fraction was

Table 8. Concentrations of Components Used in SY1-SIM-92A Simulated Waste

<u>Component</u>	<u>M (mole/L)</u>	<u>Wt%</u>
Na ₃ HEDTA	0.205	4.99
NaCl	0.526	1.97
Na ₃ PO ₄ • 12 H ₂ O	0.179	4.36
NaNO ₂	3.95	17.45
NaNO ₃	2.2	11.97
Na ₂ CO ₃	0.4	2.71
NaF	0.1	0.27
Na ₂ SO ₄	0.032	0.29
CaCl ₂	0.0083	0.06
KCl	0.146	0.7
Cr(NO ₃) ₃ • 9 H ₂ O	0.1051	2.69
Cu(NO ₃) ₂ • 2.5 H ₂ O	0.0002	0.0
Fe(NO ₃) ₃ • 9 H ₂ O	0.0074	0.19
Ni(NO ₃) ₂ • 6 H ₂ O	0.0021	0.04
NaOH	2.45	6.28
NaAlO ₂ • 0.21 NaOH • 1.33 H ₂ O	2.05	15.1
H ₂ O		<u>30.93</u>
Total		100.0

found to contain 0.8 ± 0.1 wt% TOC. These measured TOC values are slightly higher than the quantity originally added to the simulant mixture (68.5 wt% supernatant liquid $\times$ 2.2 ± 0.2 wt% TOC + 31.5 wt% settled solids $\times$ 0.8 ± 0.1 wt% TOC = 1.76 ± 0.18 wt% TOC; the TOC of the original, unseparated sample was 1.57 wt%).

The supernatant liquid fraction contained a greater share of the trisodium HEDTA than might be expected on the basis of the water content alone. The ratio of trisodium HEDTA in the supernatant liquid to that in the settled solids is $2.2 \pm 0.2 / 0.8 \pm 0.1 \approx 2.8 \pm 0.4$ (root-means-square error estimate). The ratio of water content in the supernatant liquid to that in the settled solids is $48 \pm 3 / 29 \pm 2 = 1.66 \pm 0.15$ (root-means-square error estimate). This difference is attributed to the presence of waters of hydration associated with solid phases in the settled solids fraction, which are less able to dissolve trisodium HEDTA than free water.

4.2 Gas Generation Results

Gas generation tests and product analyses were performed using methods previously described by Bryan and Pederson (1994). Tests were performed in 1 L capacity stainless steel vessels, using simulant sample sizes of approximately 250 mL. The reaction vessels were equipped with pressure

transducers to allow total gas production to be followed continuously. Samples were heated to either 60 or 90°C. Samples were either run under thermal only conditions or irradiated by ^{60}Co gamma source at 8.7×10^4 R/h. Gas samples were withdrawn at the end of approximately 500-hour tests for mass spectrometry analysis. TOC analyses were also performed at the end of the tests.

We did not include a true control in this set of experiments. However, gas generation from the SY1-SIM-92A simulant containing no HEDTA (or any other organic) was reported in Bryan and Pederson (1994). Nitrous oxide and hydrogen yields were approximately three orders of magnitude smaller when HEDTA was absent at 90°C, no radiation. The difference was approximately three orders of magnitude for nitrous oxide yields at 90°C and a dose rate of 0.6M R/h, and approximately a factor of 5 for hydrogen.

Within experimental error, there was no change in TOC as a result of heating or gamma irradiation. TOC concentrations for the settled solids and supernatant liquid fractions are given in Table 9. These results are also given in Figures 12 and 13 for the supernate and settled solids fractions, respectively. The present results indicate only that very little, if any, trisodium HEDTA was converted to carbonate. No information on the partial oxidation of this complexant is provided by TOC values. Specific organic analyses were not performed on these samples to determine the extent of trisodium HEDTA degradation to other organic species.

With few exceptions, the supernate fraction yielded more gaseous products than did the settled solids fraction, both under thermal and combined thermal and radiolytic conditions. Gas generation results for the supernatant liquid and settled solids fractions are summarized in Table 10 (60°C results) and Table 11 (90°C results), expressed in moles of gas/kg simulant/day. Exceptions were found for oxygen and NO_x , which were produced in extremely small quantities and are subject to relatively large errors. The supernatant liquid contains significantly more trisodium HEDTA per unit mass than does the settled solids fraction, leading to higher rates of flammable gas production. For a given simulant composition, a direct relation between the concentration of organic complexants and the thermal production of flammable gases has been reported previously (Delegard 1980; Ashby et al. 1993, 1994b; Bryan and Pederson 1994). An important radiolytic mechanism for hydrogen production involves the abstraction of a hydrogen atom from an organic molecule by a hydrogen radical; hydrogen production rates by this mechanism should also be directly proportional to the concentration of trisodium HEDTA. Hydrogen may also be produced by the radiolysis of water in the absence of organic compounds, however, which would be independent of the concentration of trisodium HEDTA (Meisel et al. 1993).

Normalization of gas generation yields by the TOC content of the supernatant liquid and settled solids fractions led to more similar total quantities of gases produced by the two fractions. These results are included in Tables 10 and 11, expressed in moles of gas/kg simulant/day/TOC content in wt%. For tests conducted at 60°C with and without gamma irradiation, the supernate produced approximately 50% more moles of gas than did the settled solids fraction, when normalized by the TOC content. At 90°C without gamma irradiation and for a dose rate of 8.70×10^4 R/h, the total moles of gases produced by the two fractions were identical within experimental error, again when normalized by the TOC content. At 90°C and a gamma dose rate of 4.4×10^5 R/h, the settled solids fraction gave a normalized gas production rate approximately double that obtained from the supernate.

Table 9. TOC Analyses of Solid and Supernate Fractions of Tank 241-SY-101 Simulated Waste SY1-SIM-92A with Added HEDTA (heating and irradiation time was 450 hours)

		Supernate			
		60°C	60°C	90°C	90°C
	<u>control</u>	<u>no γ</u>	<u>8.7 x 10⁴R/h</u>	<u>no γ</u>	<u>8.7 x 10⁴R/h</u>
TOC (wt%)	2.2	2.2	2.1	2.0	2.0

		Centrifuged solids			
		60°C	60°C	90°C	90°C
	<u>control</u>	<u>no γ</u>	<u>8.7 x 10⁴R/h</u>	<u>no γ</u>	<u>8.7 x 10⁴R/h</u>
TOC (wt%)	0.80	0.88	0.91	0.84	0.70

Figure 12. TOC Values of Supernate Fraction of SY1-SIM-92A with Added HEDTA Before and After Heat and Irradiation Treatment

Figure 13. TOC Values of Solid Fraction of SY1-SIM-92A with Added HEDTA Before and After Heat and Irradiation Treatment

Normalization of gas generation yields by the TOC content is considered to be appropriate under thermal-only conditions, for which first-order kinetic behavior with respect to soluble organic components has been reported (Delegard 1980; Ashby et al. 1993, 1994b; Bryan and Pederson 1994). Under radiolytic conditions, normalization by the TOC content is less appropriate, because gas-producing reactions occur that are not directly limited by the concentration of organics. Hydrogen is produced by both the direct radiolysis of water and the abstraction of hydrogen atoms from an organic molecule by hydrogen radicals (Meisel et al. 1993). Nitrous oxide production under radiolytic conditions derives principally from nitrite ions; organic components are required as reducing agents but are not involved in the rate-determining step (Meisel et al. 1993). Under radiolytic conditions, the lack of scaling of the rate of gas production with the concentration of trisodium HEDTA is most apparent for tests conducted at the highest gamma dose rate.

There are differences in the stoichiometry of gases produced in the supernatant liquid and settled solids fractions. At 90°C and without gamma irradiation (Table 11), the ratio of the nitrous oxide to nitrogen yields was considerably higher in the supernatant liquid sample than in the settled solids fraction. Quantities of gases generated as a function of time are given in Figure 14, emphasizing that trend. As described in Section 3, nitrogen is one of the decomposition products of nitrous oxide. Nitrous oxide decomposition is known to be catalyzed by a number of oxide surfaces, most effectively by p-type oxides (Hauffe, Glang, and Engell 1950; Dell, Stone, and Tiley 1953; Laidler 1965). Certain glass surfaces have been shown to be catalytically active in decomposing nitrous oxide (Ashby et al. 1994b). It is possible that the solid phases present in the settled solids fraction catalyzed the decomposition of nitrous oxide to nitrogen and oxygen. At 90°C with no radiation present, the oxygen

Table 10. Gas Generation Results from Waste Simulant SY1-SIM-92A with Trisodium HEDTA at 60°C

Reaction Conditions: 60°C, 0R/h							
Supernate Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)							
<u>Time (h)</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>N₂O</u>	<u>CH₄</u>	<u>NO_x</u>	<u>total gas</u>
500	5.2E-04	7.4E-04	1.8E-04	1.1E-05	0.0E+0	0.0E+0	1.4E-03
mol/Kg/day	2.5E-05	3.6E-05	8.5E-06	5.3E-07	0.0E+0	0.0E+0	6.9E-05
mol/Kg/day/TOC	1.1E-05	1.6E-05	3.9E-06	2.4E-07	0.0E+0	0.0E+0	3.2E-05
Reaction Conditions: 60°C, 0R/h							
Centrifuged Solids Fraction; TOC = 0.8 wt%; Gas Production (mol/kg)							
<u>Time (h)</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>N₂O</u>	<u>CH₄</u>	<u>NO_x</u>	<u>total gas</u>
500	1.5E-04	3.1E-04	9.5E-06	4.5E-06	0.0E+0	0.0E+0	3.4E-04
mol/Kg/day	7.0E-07	1.5E-05	4.6E-07	2.1E-07	0.0E+0	0.0E+0	1.6E-05
mol/Kg/day/TOC	8.7E-07	1.8E-05	5.7E-07	2.7E-07	0.0E+0	0.0E+0	2.0E-05
Sample Treatment: 60°C, 8.70x10 ⁴ R/h							
Supernate Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)							
<u>Time (h)</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>N₂O</u>	<u>CH₄</u>	<u>NO_x</u>	<u>total gas</u>
500	4.5E-03	4.4E-03	4.6E-04	1.9E-02	5.0E-06	0.0E+0	2.8E-02
mol/Kg/day	2.2E-04	2.1E-04	2.2E-05	9.1E-04	2.4E-06	0.0E+0	1.4E-03
mol/Kg/day/TOC	9.9E-05	9.6E-05	1.0E-05	4.1E-04	1.1E-06	0.0E+0	6.2E-04
Sample Treatment: 60°C, 8.70x10 ⁴ R/h							
Centrifuged Solids Fraction; TOC = 0.8 wt%							
	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>	<u>N₂O</u>	<u>CH₄</u>	<u>NO_x</u>	<u>total gas</u>
mol/500h	1.4E-03	1.8E-03	1.4E-05	4.7E-03	1.7E-05	0.0E+0	7.9E-03
mol/Kg/day	6.9E-05	8.5E-05	6.8E-07	2.2E-04	5.8E-07	0.0E+0	3.8E-04
mol/Kg/day/TOC	8.6E-05	1.1E-04	8.6E-07	2.8E-04	7.2E-07	0.0E+0	4.7E-04

Table 11. Gas Generation Results from Waste Simulant SY1-SIM-92A Containing Trisodium HEDTA at 90°C

Reaction Conditions: 90°C, 0R/h								
Supernate Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	NH ₃	total gas
287	1.79E-03	5.98E-03	8.75E-05	7.40E-03	0	3.64E-05	0	1.5E-02
575	3.29E-03	1.70E-02	1.17E-04	2.41E-02	2.10E-06	9.88E-05	3.66E-04	4.5E-02
mol/kg/day	1.37E-04	7.09E-04	4.88E-06	1.01E-03	8.77E-08	4.12E-06	1.53E-05	1.9E-03
mol/kg/day/TOC	6.23E-05	3.22E-04	2.22E-06	4.59E-04	3.99E-08	1.87E-06	6.95E-06	8.5E-04
Centrifuged Solids Fraction; TOC = 0.8 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	NH ₃	total gas
287	5.69E-04	2.88E-03	1.60E-04	1.08E-03	0	2.11E-05	0	4.7E-03
575	2.31E-03	8.97E-03	6.84E-04	5.10E-03	1.37E-06	5.62E-05	2.33E-04	1.7E-02
mol/kg/day	9.65E-05	3.75E-04	2.86E-05	2.13E-04	5.72E-08	2.35E-06	9.75E-06	7.3E-04
mol/kg/day/TOC	1.21E-04	4.69E-04	3.58E-05	2.63E-04	8.00E-08	2.94E-06	1.22E-05	9.0E-04
Reaction conditions: 90°C, 4.4 x 10 ⁵ R/h								
Supernate Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	NH ₃	total gas
287	2.55E-02	1.30E-02	1.95E-05	7.85E-02	2.46E-04	8.70E-05	0	1.7E-01
575	3.48E-02	6.92E-02	2.97E-05	1.85E-01	4.72E-04	4.90E-04	1.14E-02	3.0E-01
mol/kg/day	1.45E-03	2.89E-03	1.24E-06	7.70E-03	1.97E-05	2.05E-05	4.76E-04	1.3E-02
mol/kg/day/TOC	6.59E-04	1.31E-03	5.64E-07	3.50E-03	8.95E-06	9.32E-06	2.16E-04	5.7E-03
Centrifuged Solids Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	NH ₃	total gas
287	2.41E-02	1.06E-02	3.50E-05	6.46E-02	4.80E-05	1.34E-04	0	1.0E-01
575	4.24E-02	3.29E-02	6.32E-05	1.29E-01	1.12E-04	4.26E-04	5.89E-03	2.1E-01
mol/kg/day	1.77E-03	1.37E-03	2.64E-06	5.38E-03	4.67E-06	1.78E-05	2.46E-04	8.8E-03
mol/kg/day/TOC	2.21E-03	1.71E-03	3.30E-06	6.73E-03	5.84E-06	2.23E-05	3.08E-04	1.1E-02
Reaction Conditions: 90°C, 8.70x10 ⁴ R/h								
Supernate Fraction; TOC = 2.2 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	total gas	
500	3.7E-02	1.8E-02	3.9E-05	5.9E-02	9.1E-05	0.0E+0	1.1E-01	
mol/Kg/day	1.8E-03	8.5E-04	1.9E-06	2.8E-03	4.4E-06	0.0E+0	5.5E-03	
mol/Kg/day/TOC	8.1E-04	3.9E-04	8.5E-07	1.3E-03	2.0E-06	0.0E+0	2.5E-03	
Centrifuged Solids Fraction; TOC = 0.8 wt%; Gas Production (mol/kg)								
Time (h)	H ₂	N ₂	O ₂	N ₂ O	CH ₄	NO _x	total gas	
500	1.2E-02	4.5E-03	4.5E-05	2.6E-02	5.7E-05	0.0E+0	4.3E-02	
mol/Kg/day	5.9E-04	2.2E-04	2.2E-06	1.3E-03	2.7E-06	0.0E+0	2.1E-03	
mol/Kg/day/TOC	7.4E-04	2.7E-04	2.7E-06	1.6E-03	3.4E-06	0.0E+0	2.6E-03	

content was also somewhat higher for the settled solids fraction than for the supernatant liquid, consistent with the above discussion. The concentration of oxygen determined in these experiments does not provide a good means to estimate the quantity of nitrous oxide decomposed. This is because oxygen is consumed in reaction with HEDTA. There is no obvious method to calculate a mass balance here, because we don't know the precise speciation of HEDTA breakdown products.

Under radiolytic conditions, differences in the stoichiometry of product gases were less pronounced than for thermal-only conditions. Quantities of gases generated by combined thermal and radiolytic reactions as a function of time are given in Figure 15. Total gas production for a gamma dose rate of 4.4×10^5 R/h at 90°C was approximately a factor of ten greater than it was in the absence of radiation (compare Figures 14 and 15). The apparently much higher production rates of these gases under combined thermal and radiolytic conditions are sufficient to mask kinetically slower decomposition reactions involving nitrous oxide in these tests. We do not know why the hydrogen yields appeared to decrease with increased dose rate for the supernate fractions at 90°C (Table 11). Concentrations obtained for other products are as expected. We think that the data point may well be in error.

The main point of these tests was to directly compare rates of gas generation in the settled solids layer and in the supernatant liquid. As described above, the fractions were separated at 25°C, characterized, and then used in gas generation tests. This method allowed us to normalize the results to the amount of HEDTA in each fraction. The conclusion is that the solids do not appear to substantially alter reaction rates. Perhaps we would see differences for other organics, but none was seen for the quite reactive HEDTA.

It is somewhat difficult to compare these results directly with those from other simulants reported previously (Bryan and Pederson 1994). In this earlier report, the homogeneous simulants were much less concentrated than the heterogeneous simulants. The homogeneous simulants contained only the major components, i.e., sodium hydroxide, nitrate, nitrite, aluminate, and carbonate. In the present study, the SY1-SIM-92A simulant was used. This simulant contains the principal components cited above in addition to a variety of transition metals, chloride, sulfate, and phosphate. The minor components were shown by Bryan and Pederson (1994) to have a significant impact on gas product yields.

In summary, although the presence of solid phases does not appear to substantially alter the overall quantity of gases produced, those solids may catalyze decomposition reactions that can alter gas product distributions. The kinetics of nitrous oxide decomposition to yield nitrogen and oxygen are expected to be most affected. It is cautioned that the present study included only trisodium HEDTA, whereas many other organic compounds and fragments are known to be present in the actual wastes. Greater interactions between other organic constituents and solid phases may occur, leading to much different gas generation kinetics in the supernatant liquid and settled solids fractions.

Figure 14. Gas Generation Data from Supernate and Solid Fractions of Centrifuged SY1-SIM-92A Waste Simulant with Added HEDTA (conditions: 90°C, 575 hour reaction time)

Figure 15. Gas Generation Data from Supernate and Solid Fractions of Centrifuged SY1-SIM-92A Waste Simulant with Added HEDTA (reaction conditions: 90°C, 4.4×10^5 R/h, 575 hour reaction time)

5.0 Summary and Conclusions

Gas Reactions under Thermal and Combined Thermal and Radiolytic Conditions: The reactivities of essentially pure nitrous oxide, of nitrous oxide and hydrogen mixtures, and of nitrogen and hydrogen mixtures were evaluated under thermal and combined thermal and radiolytic conditions. Tests were performed in stainless steel vessels in the temperature range of 60 to 150°C, with ^{60}Co gamma irradiation doses from 0 to more than 100 Mrad and reaction times extending to approximately 500 hours. These tests did not include simulated waste mixtures, to avoid complications associated with additional flammable gas production.

Nitrous oxide, among the more stable oxides of nitrogen, decomposed under radiolytic conditions to yield nitrogen, oxygen, and nitrogen dioxide. Essentially independent of temperature in the 60 to 150°C range, $G(-\text{N}_2\text{O})$ was determined to be -12 molecules/100 eV, in good agreement with literature values. Nitrogen dioxide formation was favored at the lowest temperatures and nitrogen favored at the highest temperatures. Under thermal-only conditions in stainless steel vessels, nitrous oxide decomposition was not observed. Based on literature results, at the temperatures of these experiments, the thermal decomposition of nitrous oxide in the gas phase should be far too slow to be observed. Catalyzed decomposition may occur; research at GIT and elsewhere has shown that nitrous oxide is decomposed on glass surfaces at similar temperatures. Present results show that stainless steel is not an effective nitrous oxide decomposition catalyst, however. Assuming a gamma dose rate of 1000 R/h in the actual wastes, and assuming that nitrous oxide composes ≈ 30 percent of the gases trapped in the nonconvecting layer, it is estimated that ≈ 1 percent of the retained nitrous oxide could be consumed by these radiolytic reactions per year.

Nitrous oxide may also be consumed in reactions with other gaseous species. Nitrous oxide reacts with hydrogen to yield nitrogen, oxygen, and ammonia under thermal and combined thermal and radiolytic conditions. Nitrous oxide consumption was accelerated by the presence of hydrogen, consistent with the recent findings of Hertzberg and Zlochower (1994). Essentially independent of temperature, $G(-\text{N}_2\text{O})$ was determined to be -30 molecules/100 eV, approximately 2.5 times greater than that determined in the absence of hydrogen.

Ammonia was the principal product of nitrogen and hydrogen reactions. Radiolytic ammonia yields showed a strong inverse relation to radiation dose. For low radiation doses, $G(\text{NH}_3)$ was nearly 1 molecule/100 eV, in good agreement with literature values. However, this yield decreased to approximately 0.01 molecules/100 eV for doses greater than 10 Mrad. From literature results, the value of $G(-\text{NH}_3)$ is known to be as much as a factor of ten greater than $G(\text{NH}_3)$, depending on temperature and gas partial pressures. As the concentration of NH_3 increased in the gas mixture, so did the relative importance of ammonia decomposition back to nitrogen.

Comparison of Gas Generation in Homogeneous Liquid and Centrifuged Solids Fraction of a Simulated Waste Mixture: Nearly identical overall rates of gas generation were obtained from the homogeneous liquid fraction and centrifuged solids fraction of a simulated waste under thermal and combined thermal and radiolytic conditions, when corrected for the organic content of the two fractions. Trisodium HEDTA was the sole organic constituent of the simulated waste, which was partitioned between the two fractions in a manner roughly proportional to the water content. Although the

total quantities of gases produced were similar, there were differences in the stoichiometry of the product. Gases produced by the centrifuged solids fraction contained higher nitrogen concentrations than did mixtures produced by the homogeneous liquid. Catalysis of nitrous oxide decomposition reactions by solid phases may have been responsible for these differences.

6.0 References

- Allemann, R. T. 1994. *Some Theories of Dissolved Gas Release from Tank 241-SY-101*. PNL-10091, Pacific Northwest Laboratory, Richland, Washington.
- Anderson, A. R. 1968. *Fundamental Processes in Radiation Chemistry*. P. Ausloos, ed. John Wiley and Sons, New York, p. 281.
- Arnold, E. A., and R. E. Burk. 1932. "Thermal Decomposition of Ammonia on the Surface of Osmium." *J. Amer. Chem. Soc.*, 54:23-32.
- Ashby, E. C., C. Jonah, D. Meisel, L. R. Pederson, and D. M. Strachan. 1992. *Gas Generation and Retention in Tank 241-SY-101: A Summary of Laboratory Studies, Tank Data, and Information Needs*. PNL-8124, Pacific Northwest Laboratory, Richland, Washington.
- Ashby, E. C., F. Doctorovich, C. L. Liotta, H. M. Neumann, E. K. Barefield, A. Konda, K. Zhang, J. Hurley, and D. D. Siemer. 1993. "Concerning the Formation of Hydrogen in Nuclear Waste. Quantitative Generation via a Cannizzaro Intermediate." *J. Am. Chem. Soc.*, 115:1171-1173.
- Ashby, E. C., E. K. Barefield, C. L. Liotta, H. M. Neumann, F. Doctorovich, A. Konda, K. Zhang, J. Hurley, D. Boatwright, D. A. Annis, G. Pansino, M. Dawson, and M. Juliao. 1994a. "Mechanistic Studies Related to the Thermal Chemistry of Simulated Nuclear Wastes that Mimic the Contents of a Hanford Site Double-Shell Tank." *Am. Chem. Soc. Symp. Ser.*, 554:249-284.
- Ashby, E. C., D. A. Annis, E. K. Barefield, D. Boatwright, F. Doctorovich, C. L. Liotta, H. M. Neumann, A. Konda, C. F. Yao, K. Zhang, and N. G. McDuffie. 1994b. *Synthetic Waste Chemical Mechanism Studies*. WHC-EP-0823, Westinghouse Hanford Company, Richland, Washington.
- Babad, H., G. D. Johnson, J. A. Lechelt, D. A. Reynolds, L. R. Pederson, D. M. Strachan, D. Meisel, C. D. Jonah, and E. C. Ashby. 1991. *Evaluation of the Generation and Release of Flammable Gases in Tank 241-SY-101*. WHC-EP-0517, Westinghouse Hanford Company, Richland, Washington.
- Babad, H., G. D. Johnson, D. A. Reynolds, and D. M. Strachan. 1992. *"Understanding of Cyclic Venting Phenomena in Hanford Site High-Level Waste Tanks: The Evaluation of Tank 241-SY-101."* WHC-SA-1364-FP, Westinghouse Hanford Company, Richland, Washington.
- Baer, D. R., and L. S. Dake. 1986. *Oxidation of Metals and Associated Mass Transport*. M. A. Dayananda, S. J. Rothman, and W. E. King, eds. Metallurgical Society of AIME, New York, p. 185.
- Bottomley, F., and R. C. Burns. 1979. *Treatise on Nitrogen Fixation*. Wiley Interscience, New York, p. 50.
- Bou-Hamra, W. S. 1988. *Formation of Ammonium Nitrate Aerosols by Gas-Phase Reaction of Ammonia and Nitrogen Dioxide*. Ph.D. Dissertation, Oklahoma State University, Stillwater, Oklahoma.

Briant, C. L., and R. A. Mulford. 1982. "Surface Segregation in Austenitic Stainless Steel." *Met. Trans. A.*, 13A:745-752.

Bryan, S. A., L. R. Pederson, J. L. Ryan, R. D. Scheele, and J. M. Tingey. 1992. *Slurry Growth, Gas Retention, and Flammable Gas Generation by Hanford Radioactive Waste Tanks: Synthetic Waste Studies*. PNL-8169, Pacific Northwest Laboratory, Richland, Washington.

Bryan, S. A., L. R. Pederson, and R. D. Scheele. 1992. "Crust Growth and Gas Retention in Synthetic Hanford Wastes." *Proceedings of the Waste Management '92 Conference*, 1:829-834. American Nuclear Society, Las Vegas, Nevada.

Bryan, S. A., and L. R. Pederson. 1992. In *Minutes of the Tank Waste Science Panel Meeting March 25-27, 1992*. W. W. Schulz and D. M. Strachan, eds. PNL-8278, Pacific Northwest Laboratory, Richland, Washington.

Bryan, S. A., L. R. Pederson, R. D. Scheele, and S. R. Adami. 1993. In *Proceedings of the 4th Annual International Conference on High Level Radioactive Waste Management*, 2:1348. American Nuclear Society, Las Vegas, Nevada.

Bryan, S. A., and L. R. Pederson. 1994. *Composition, Preparation, and Gas Generation Results from Simulated Wastes of Tank 241-SY-101*. PNL-10075, Pacific Northwest Laboratory, Richland, Washington.

Cotton, F. A., and G. Wilkinson. 1980. *Advanced Inorganic Chemistry, 4th Edition*, p. 418.

CRC Handbook of Radiation Chemistry. 1986. Chemical Rubber Company, Cleveland, Ohio, p. 607.

Delegard, C. 1980. *Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101*. RHO-LD-124, Rockwell International, Richland, Washington.

Dell, R. M., F. S. Stone, and P. F. Tiley. 1953. "The Decomposition of Nitrous Oxide on Cuprous Oxide and Other Oxide Catalysts." *Trans. Faraday Soc.*, 49:201-209.

Doremus, R. H. 1973. *Glass Science*. John Wiley and Sons, New York, p. 102.

Engell, H. J., and K. Hauffe. "Der Einfluß der Elektronenfehlordnung oxydischer Katalysatoren auf die Zerfallsgeschwindigkeit des Stickoxyduls." 1953. *Z. Elektrochem.*, 57:776-778.

Garner, W. E., T. J. Gray, and F. S. Stone. 1950. "Reactions on the Surface of Copper Oxide." *Discussions Faraday Soc.*, 8:246-250.

Gauglitz, P. A., R. R. Shah, and R. L. Davis. 1994a. *Gas Distribution Effects on Waste Properties: Viscosities of Bubbly Slurries*. PNL-10112, Pacific Northwest Laboratory, Richland, Washington.

Gauglitz, P. A., L. A. Mahoney, D. P. Mendoza, and M. C. Miller. 1994b. *Mechanisms of Gas Bubble Retention*. PNL-10120, Pacific Northwest Laboratory, Richland, Washington.

Harteck, P., and S. Dondes. "Nitrous Oxide Dosimeter for High Levels of Betas, Gammas, and Thermal Neutrons." 1956. *Nucleonics*, 14(3):66-72.

Hauffe, K., R. Glang, and H. J. Engel. "The Effect of the Electron Disorder Structure of Oxide Catalysts on the Decomposition of Nitrous Oxide." 1950. *Z. Physik. Chem.*, 201:223.

Hearne, J. A., and R. W. Hummel. 1961. "Nitrous Oxide as a Dosimeter for Ionizing Radiations." *Radiation Res.*, 15:254-257.

Herting, D. L., D. B. Bechtold, B. A. Crawford, T. L. Welsh, and L. Jensen. 1992a. *Laboratory Characterization of Samples Taken in May 1991 from Hanford Tank 241-SY-101*. WHC-SE-WM-DTR-024, Westinghouse Hanford Company, Richland, Washington.

Herting, D. L., D. B. Bechtold, B. E. Hey, B. D. Keele, L. Jensen, and T. L. Welsh. 1992b. *Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101*. WHC-SD-WM-DTR-026 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Hertzberg, M., and I. A. Zlochower. 1994. In *Proceedings of the 25th International Symposium on Combustion*. The Combustion Institute, Pittsburgh, Pennsylvania, p. 254.

Hibben, J. H. 1928. "The Low Pressure Decomposition of Nitric and Nitrous Oxides." *J. Amer. Chem. Soc.*, 50:940-950.

Hinshelwood, C. N., and R. T. Burke. 1925. "The Thermal Decomposition of Ammonia on Various Surfaces." *J. Chem. Soc.*, 127:1105-1117.

Hinshelwood, C. N., and C. R. Pritchard. 1925a. "The Catalytic Decomposition of Nitrous Oxide on the Surface of Gold: a Comparison with the Homogeneous Reaction." *Proc. Royal Soc. (London)*, A108:211-215.

Hinshelwood, C. N., and C. R. Pritchard. 1925b. "A Comparison Between the Homogeneous Thermal Decomposition of Nitrous Oxide and its Heterogeneous Catalytic Decomposition on the Surface of Platinum." *J. Chem. Soc.*, 127:327-336.

Homann, K. H., and A. Haas. 1972. In *Comprehensive Chemical Kinetics, Vol. 4: Decomposition of Inorganic and Organometallic Compounds*, eds. C. H. Bamford and C. F. H. Tipper, p. 1.

Hutchinson, W. H., and C. N. Hinshelwood. 1926. "The Interaction of Hydrogen and Nitrous Oxide on the Surface of Gold." *J. Chem. Soc.*, 129:1556-1559.

Jacobs, T. A. 1963. "Further Shock-Tube Studies by Infrared Emission of the Decomposition of Ammonia." *J. Phys. Chem.*, 67:665-667.

Johnson, G. R. A. 1962. "The Nitrous Oxide Radiation Dosimeter." *J. Inorg. Nucl. Chem.*, 24:461-468.

Johnson, G. R. A. 1973. *Radiation Chemistry of Nitrous Oxide Gas. Primary Processes, Elementary Reactions, and Yields*. NSRDS-NBS 45, U.S. Department of Commerce-National Bureau of Standards, Washington, D.C.

Johnston, H. S. 1951. "Interpretation of the Data on the Thermal Decomposition of Nitrous Oxide." *J. Chem. Phys.*, 19:663-668.

Jones, K. 1975. In *Comprehensive Inorganic Chemistry*. J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, eds. Pergamon Press, New York, p. 147.

Kaufman, F., N. J. Gerri, and R. E. Bowman. 1956. "Role of Nitric Oxide in the Thermal Decomposition of Nitrous Oxide." *J. Chem. Phys.*, 25:106-115.

Kunsman, C. H. 1928. "The Thermal Decomposition of Ammonia in Tungsten, Molybdenum and Nickel. I." *J. Amer. Chem. Soc.*, 50:2100-2113.

Laidler, K. J. 1965. *Chemical Kinetics*. McGraw-Hill, New York, p. 296.

Lindars, F. J. and C. N. Hinshelwood. 1955a. "The Thermal Decomposition of Nitrous Oxide I. Secondary Catalytic and Surface Effects." *Proc. Royal Soc. Series A*, 231:162-178.

Lindars, F. J. and C. N. Hinshelwood. 1955b. "The Thermal Decomposition of Nitrous Oxide II. Influence of Added Gases and a Theory of the Kinetic Mechanism." *Proc. Royal Soc. Series A*, 231:178-197.

Los Alamos National Laboratory (LANL). 1994. *A Safety Assessment for Proposed Pump Mixing Operations to Mitigate Episodic Gas Releases in Tank 241-SY-101: Hanford Site, Richland, Washington*. LA-UR-92-3196 Rev. 9, Los Alamos National Laboratory, Los Alamos, New Mexico.

Meisel, D., H. Diamond, E. P. Horwitz, C. D. Jonah, M. S. Matheson, M. C. Sauer Jr., and J. C. Sullivan. 1991. *Radiation Chemistry of Synthetic Waste*. ANL-91/40, Argonne National Laboratory, Argonne, Illinois.

Meisel, D., H. Diamond, C. D. Jonah, M. C. Sauer, Jr., J. C. Sullivan, F. Barnabas, E. Cerny, and Y. D. Cheng. 1992. "Radiolytic and Radiolytically Induced Generation of Gases in Simulated Mixed Waste Solutions." In *Proceedings of Waste Management '92*, 1:859. American Nuclear Society and International Atomic Energy Agency.

Meisel, D., C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr. 1993. *Radiolytic and Radiolytically Induced Generation of Gases From Synthetic Wastes*. ANL-93/43, Argonne National Laboratory, Argonne, Illinois.

Melia, T. P. 1965. "Decomposition of Nitric Oxide at Elevated Pressures." *J. Inorg. Nucl. Chem.*, 27:95-98.

Melville, H. W. 1934. "The Kinetics of the Reaction between Hydrogen and Nitrous Oxide. Part II." *Proc. Roy. Soc. A*, 146:737-775.

Michel, K. W. and H. G. Wagner. 1965. *Tenth International Symp. on Combustion*. The Combustion Institute, Pittsburgh, Pennsylvania, p. 353.

Norton, J. D., and L. R. Pederson. 1994. *Ammonia in Simulated Hanford Double-Shell Tank Wastes: Solubility and Effects on Surface Tension*. PNL-10173, Pacific Northwest Laboratory, Richland, Washington.

Orth, R. J., A. J. Schmidt, A. H. Zacher, M. R. Elmore, T. R. Hart, J. C. Poshusta, G. G. Neuenschwander, E. O. Jones, and S. R. Gano. 1993. *Organic Destruction Technology Development Task Annual Report - FY 1993: Hydrothermal Processing of Hanford Tank Waste*. PNL-10108, Pacific Northwest Laboratory, Richland, Washington.

Pederson, L. R., and S. A. Bryan. 1994. *Assessment of the Potential for Ammonium Nitrate Formation and Reaction in Tank 241-SY-101*. PNL-10067, Pacific Northwest Laboratory, Richland, Washington.

Preston, K. F., and R. J. Cvetanovic. 1972. In *Comprehensive Chemical Kinetics*, Vol. 4: *Decomposition of Inorganic and Organometallic Compounds*, p. 47.

Reynolds, D. A., D. D. Siemer, D. M. Strachan, and R. W. Wallace. 1991. *A Survey of Available Information on Gas Generation in Tank 241-SY-101*. PNL-7520, Pacific Northwest Laboratory, Richland, Washington.

Samsonov, G. V. 1973. *The Oxide Handbook*. IFI-Plenum, New York, p. 210.

Sax, N. I. 1979. *Dangerous Properties of Industrial Materials, 5th Edition*. Van Nostrand Reinhold Company, New York, p. 325.

Schmidt, A. J., E. O. Jones, R. J. Orth, M. E. Elmore, D. C. Meng, G. G. Neuenschwander, T. R. Hart. 1993. *Preliminary Conceptual Design for the Destruction of Organic/Ferrocyanide Constituents in the Hanford Tank Waste with Low Temperature Hydrothermal Processing*. PNL-SA-23181, Pacific Northwest Laboratory, Richland, Washington.

Schmidt, A. J., M. E. Elmore, R. J. Orth, R. O. Jones, A. J. Zacher, T. R. Hart, G. G. Neuenschwander, and J. C. Poshusta. 1994. "Organic Destruction to Enhance the Separation of Strontium in Radioactive Wastes," In *Metals and Materials Waste Recovery and Remediation*, K. C. Liddell, R. G. Bautista, and R. J. Orth, Editors, the Minerals, Metals, and Materials Society, pp. 151-162.

Schulz, W. W., and D. M. Strachan. 1992. *Minutes of the Tank Waste Science Panel Meeting, March 25-27, 1992*. PNL-8278, Pacific Northwest Laboratory, Richland, Washington.

Schumpe, A. 1993. "The Estimation of Gas Solubilities in Salt Solutions." *Chem. Eng. Sci.*, 48:153-158.

Schwab, G. M., R. Stager, and H. H. von Baumbach. 1933. "Die Stickoxydul Spaltenoe Wirkung von Metalloxyden und ihr Gang im Periodischen System." *Z. Physik. Chem.*, B21:65-83.

Simpson, R. E. 1961. "Current Developments in the Use of Nitrous Oxide in the Radiation Dosimetry Associated with the Radiation Effects Reactor." *Health Physics*, 8:143-154.

Sorokin, Y. A., and S. Y. Pshezhetskii. 1964. "Decomposition of Ammonia by γ -Radiation." *Russ. J. Phys. Chem.*, 38(3):434-436.

Spinks, J. T. W., and R. J. Woods. 1990. *An Introduction to Radiation Chemistry*, John Wiley and Sons, New York, p. 210.

Strachan, D. M., and W. W. Schulz. 1993. *Minutes of the Tank Waste Science Panel Meeting January 12-13, 1993*. PNL-8845, Pacific Northwest Laboratory, Richland, Washington.

Thomas, J. M., and W. J. Thomas. 1969. *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, New York, p. 408.

Wagner, C., and K. Hauffe. 1938. "The Stationary State of Catalysts in Homogeneous Reactions." *Z. Elektrochem.*, 44:172-178.

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