LA-UR-98-4557

Title:

Literature Search on Hydrogen/Oxygen Recombination and Generation in Plutonium Storage Environments

Author(s):

Jane A. Lloyd and P. Gary Eller (Corresponding Author)
Los Alamos National Laboratory
Los Alamos, NM 87545

Lee Hyder (Retired)
Savannah River Site
Aiken, SC 29808

Submitted to:

Los Alamos
NATIONAL LABORATORY

(This page intentionally left blank.)

Contents

Executive Summary 1

Introduction 2

The Formation of Hydrogen from Liquid Water by Radiation 4

Radiation-Induced Reactions of Water Adsorbed on Solid Surfaces 5

Safety Concerns Associated with Hydrogen Accumulation 6

Catalyzed Recombination on Solid Surfaces 9

Radiation-Induced Reaction of Hydrogen and Oxygen in the Gas Phase and the Effect of Nitrogen 11

Conclusions 14

Acknowledgements 14

References 15

Additional Topical References to Hydrogen/Oxygen Reactions 18

Figures

Fig. 1. Possible surface reactions in the hydrogen/oxygen system 8

Fig. 2. Diagram of the Langmuir-Hinshelwood and the Eley-Rideal reaction mechanisms 9

(This page intentionally left blank.)

Literature Search on Hydrogen/Oxygen Recombination And Generation in Plutonium Storage Environments

Jane A. Lloyd and P. Gary Eller (Corresponding Author)

Los Alamos National Laboratory

Lee Hyder (Retired)

Savannah River Site

Executive Summary

This report evaluates the critical literature available on the gas phase recombination reactions of H_2 and O_2 in the presence and absence of ionizing radiation. The available literature on radiolysis of adsorbed water also is evaluated. The conclusion is that high H_2/O_2 pressures will not result from radiolytic and catalytic decomposition of H_2O adsorbed on PuO_2.

Introduction

Radiolytic and catalytic generation of gases in stored plutonium materials raises the concerns of pressurizing the vessel and of creating gas mixtures that may be flammable or even explosive. The most important flammable gas is hydrogen, which can be created from radiation-induced decomposition of organic material or water. In the plutonium materials proposed for long term storage, physisorbed and adsorbed water and organic materials will be minimized by high temperature calcination. However, up to 0.5 wt% of residual water on plutonium oxide and other surfaces is permissible by the current U.S. Department of Energy storage standard[1].

There are several reactions to consider in predicting hydrogen formation and destruction in stored materials. These reactions include: (1) radiolytic and catalytic decomposition of adsorbed moisture to produce hydrogen and oxygen, (2) oxidation of hydrogen by gaseous oxygen in the catalytic and radiolytic environment, (3) catalytic combination of hydrogen and oxygen on solid surfaces including the surface of plutonium oxide, and (4) oxidation of atmospheric nitrogen in the radiation field, producing nitrogen oxides, solid nitrates and nitric acid.

Recent experiments have provided a basis for the observation that oxygen generally is not produced stoichiometrically with hydrogen from moisture adsorbed on plutonium oxide[2,3]. The literature indicates that oxygen formed from water combines with plutonium dioxide to form the superstoichiometric oxide PuO_{2+x}[4]. Other experiments show that a variety of non-radioactive materials can catalyze the recombination of hydrogen and oxygen[5]. It has been suggested that plutonium oxide is an effective catalyst for H_2/O_2 recombination[3]. Measurements of headspace gases over plutonium materials stored for up to 20 years generally show a strong depletion in oxygen and enrichment in hydrogen, but no significant overpressure[6]. Experiments with PuO_2 to date do not provide a compelling basis for distinguishing between recombination induced by radiation and recombination by surface catalysis under all crcumstances, although both processes clearly can occur.

This literature review was undertaken to provide a basis for evaluating H_2/O_2 generation and reaction in plutonium oxide environments. When air is present nitrogen also may enter into radiation-induced reactions. Specifically, this literature search evaluates: (1) reactions involved in the radiolytic formation of hydrogen from liquid water, (2) radiolytic and catalytic reactions producing hydrogen from water sorbed on a solid substrate, (3) safety concerns associated with hydrogen accumulation (4) catalytic recombination of hydrogen and oxygen on solid surfaces, (5) radiation-induced recombination of hydrogen and oxygen in the gas phase, and (6) the possible involvement of nitrogen in these reactions.

This literature review was based on several sources. The most useful electronic search of radiation chemistry utilized a database maintained by the Radiation Effects Laboratory of the University of Notre Dame. Other on-line resources at the Los Alamos National Laboratory library were used as well.

Two additional electronic literature bases were the used: SciFinder and SciSearch SciFinder accesses years 1967-present and SciSearch accesses years 1974-present. The keywords that were searched included; hydrogen-oxygen-reaction, oxidation-hydrogen, and recombination-hydrogen-oxygen. The combination of hydrogen and/or oxygen was also searched with plutonium oxide, uranium oxide, 304 stainless steel, 316 stainless steel, KCl, $CaCl_2$, $MgCl_2$ and radiolysis. A manual search of Chemical Abstract citations since1976 also was performed but the relatively small number of returns from the search suggested that this approach was not very effective. Many standard texts were also consulted and are listed at the end of this report. Finally, the search included discussions with Dr. Jay

LaVerne of The Notre Dame Radiation Effects Laboratory. In general, alpha radiation studies are heavily represented in the literature prior to the Manhattan Project. Thereafter, gamma radiation studies dominate due to the availability of reactors and convenient sealed sources.

In addition to references specifically cited in this report, additional representative references by subtopic germane to this review are presented at the end of this report.

The Formation of Hydrogen from Liquid Water by Radiation

In most published studies of liquid water radiolysis, gamma radiation was utilized. Particle beams mixed reactor radiation have been used in a few cases. The irradiation of liquid water by charged particles (such as the alpha particles emitted by plutonium) produces microscopic regions along the particle pathway where a dense population of ionized and dissociated water fragments is found [7]. In neutral water, the most important such fragments are the hydroxyl radical and the hydrated electron, H_2O^-. This latter species has been characterized spectrometrically and is believed to consist of a negative charge that polarizes the water around it to create a hydration shell involving several water molecules. It is formally the basic form of atomic hydrogen and is converted to the latter in acidic solutions:

$$H_2O^- + H_3O^+ \rightarrow 2\ H_2O + H \qquad (1)$$

The interaction of two hydrated electrons in the dense track region is believed to be responsible for the radiolytic production of hydrogen, H_2, from liquid water.

$$2\ H_2O^- \rightarrow 2\ OH^- + H_2 \qquad (2)$$

The presence of dissolved species that readily react with the solvated electron in the track will reduce hydrogen production. Such species are known to include nitrate, nitrite, oxygen, and other oxidizing solutes[8]. The effect of nitrate in reducing hydrogen generation during alpha radiolysis of water has been quantified by Bibler[8].

Similar phenomena are observed with the radiolytically generated hydroxyl radical, OH[9]. Two such radicals can form hydrogen peroxide, but hydroxyl radicals also react rapidly with reducing materials such as nitrite or hydrogen gas. Back reactions of radical species with molecular radiation products can be quite fast, and correspondingly the steady-state concentrations of hydrogen and hydrogen peroxide are generally quite low[7]. For other details of the radiation chemistry of liquid water, the reader is referred to standard texts, such as that by Spinks and Woods[9].

Radiation-Induced Reactions of Water Adsorbed on Solid Surfaces

There is substantial literature on the effect of radiation on material adsorbed on solid surfaces, but only a few publications address adsorbed water. Much of the adsorbed water radiolysis literature is due to the work of investigators in the former Soviet Union. Of particular interest is reference [10], where the authors divide oxide surfaces into three categories:

1. <u>Surfaces that generate less hydrogen from adsorbed water than would be generated from the radiolysis of liquid water</u>. (G=0.01 or less, where G denotes the yield of hydrogen molecules per 100 KeV or less of absorbed energy). These surfaces generally consist of highly oxidizing materials such as MnO_2 or CrO_3, where a reduction reaction of

hydrogen or its precursors with the substrate is possible. However, the non-oxidizing compound ZnO also is placed in this low G category.

2. <u>Surfaces that yield hydrogen with G-values of approximately 1, similar to the hydrogen yield from liquid water</u>. The G-value for hydrogen from gamma radiolysis of liquid water is about 0.45, and from alpha radiolysis is slightly higher than 1. Compounds in category (2) include silica, titania, and oxides of nickel, copper and cadmium.

3. <u>Surfaces where enhanced hydrogen production is observed with G values much greater than 1</u>. These surfaces include oxides of lanthanum, magnesium, zirconium, and also aluminum and (especially) beryllium[11]. Studies at Oak Ridge[12] also placed silica gel in this category. The enhanced decomposition of water is attributed to efficient transfer of radiation energy absorbed by the substrate to the adsorbed water. In such cases the apparent G value for water radiolysis (in terms of energy absorbed directly by the water itself) can exceed 50. The data suggests that this rate applies only to the strongly adsorbed water and not to physisorbed layers of water. The enhanced production of hydrogen apparently involves the facile transfer of electrons through the crystal phase to the surface adsorbed water[12]. This effect appears to be accentuated by elevated temperatures. Taking into account the total radiation dose adsorbed by the oxide surfaces, the G values for hydrogen production are within a reasonable range compared to liquid water[12,13].

Safety Concerns Associated with Hydrogen Accumulation

Two obvious concerns when dealing with gaseous hydrogen and oxygen mixtures are deflagration and detonation. For a hydrogen-oxygen mixture in a vessel with a particular geometry and surface composition, spontaneous explosion may occur at certain values of temperature and pressure[14]. Under other conditions, slower reaction outside the detonation regime occurs. The explosion limits are typically indicated by a P-T explosion diagram, where the regions in which autoignition takes place are separated (by an S-shaped curve) from the regions where no auto ignition occurs.

Factors that affect the explosion limit include (1) total pressure, (2) mixture composition, (3) temperature, (4) dimensions of the reaction vessel and the (5) nature of the vessel inner surface. The explosion limit temperature is observed to increase in a vessel coated internally with KCl. This can be attributed to the efficient breaking of chain reaction series leading to explosion. The temperature for self-detonation is increased to greater than 450°C with a heavy surface coating of KCl[14]. In a 7.4 cm diameter glass sphere, internally coated with KCl, the explosion limit of a stoichiometric hydrogen–oxygen mixture is reached only at temperatures above 400°C[14].

Varying the composition of the salt and the dimensions of the vessel also increase/decrease the self-detonation limit in the hydrogen-oxygen reaction[14]. The smaller the vessel, the higher the pressure and temperature must be before the explosion limit is reached. However, even in rather large (500 mL) vessels, the vessel surface also may have a significant effect. This effect is due to increased reaction chain breaking at the surface of the container. The explosion limit is also shifted by changes in the salt composition, showing the strong impact of surfaces on radical chain breaking.

From the available literature and experimental and empirical observations, it is clearly not credible that the combination of temperatures, pressures and other conditions necessary for spontaneous detonation can be attained in anticipated Pu storage environments.

The lower flammability limit (LFL) of hydrogen in air is 4% at 25°C at 1 atmosphere for upward propagation of the flame in an experimental tube apparatus[15]. For downward propagation, the LFL is 9.4% at the same temperature and pressure. The LFL decreases slightly with increasing temperature. Based on recent observations, it appears very unlikely that LFL concentrations of hydrogen can be reached in anticipated Pu storage environments[3,6].

Catalyzed Recombination on Solid Surfaces

It is especially significant for this review that hydrogen/oxygen reactions at gas-solid interfaces are very important. More specifically, the recombination of H_2 and O_2 on the surface of PuO_2, common salts (KCl, NaCl, and $CaCl_2$) and stainless steel are highly relevant to plutonium storage environments. Quigley's recent paper[5] addresses these reactions in non-radiolytic environments. Only a few papers address H_2/O_2 recombination over PuO_2[2,3,4] . A few other papers have been published on relevant surface recombination reactions in the presence of common salts. For example, Smith reported that H atoms do not readily recombine to H_2 over dry KCl but O and H atoms recombine readily to form OH[16]. Other compounds (i.e., K_2CO_3,K_2SiO_3, Na_3PO_4) strongly induce H atom recombination when dry and less strongly when wet.

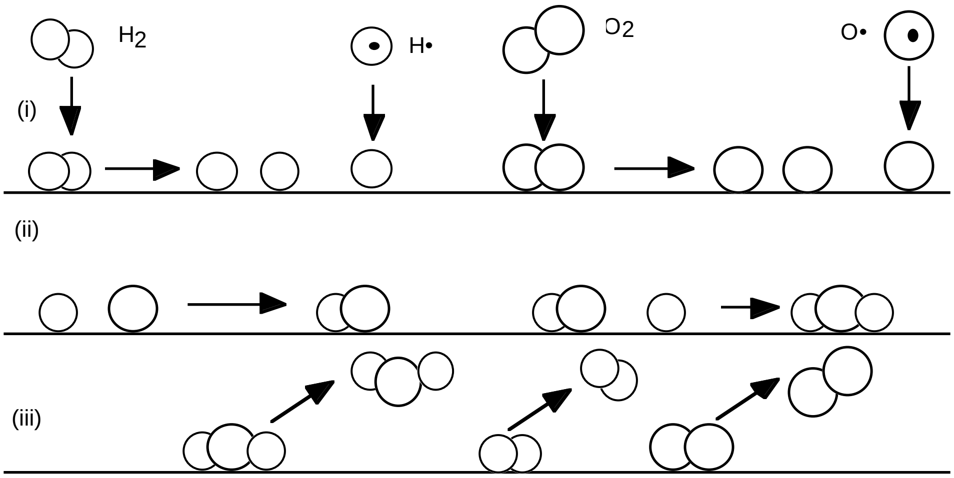

Fig. 1. Possible surface reactions in the hydrogen/oxygen system.

It is well established that surface reactions play a significant role in recombination (chain breaking) reactions of radicals. One possible surface recombination reaction mechanism for the hydrogen/oxygen system is shown in Fig. 1. In Fig. 1(i), hydrogen and oxygen (either as radicals or as molecules) approach the surface, adsorb, and dissociate to produce adsorbed H or O atoms. Adsorbed hydrogen and oxygen atoms then can react with each other to form OH water or moieties adsorbed on the surface, as shown in Fig. 1 (ii). Finally, molecular desorption as water, hydrogen or oxygen can occur (Fig. 1 (iii)). Although Fig. 1 depicts the dominant surface chemical processes that occur in the hydrogen/oxygen system, other gas phase products can form similarly from radiolysis of other adsorbed species.

Another consideration is reaction of surface adsorbed species with ions or radicals. Two relevant types of accepted generic surface reactions are depicted in Fig. 2[17]. The Langmuir-Hinshelwood mechanism, in which all molecules or atoms need to be adsorbed to the surface to react, is shown in Figure 2 (i) and was discussed above for the H_2/O_2 system. A second reaction mechanism involves the reaction of gas phase atoms (ions or radicals) with adsorbed atoms. This reaction sequence is called an Eley-Rideal mechanism and is depicted in Figure 2 (ii).

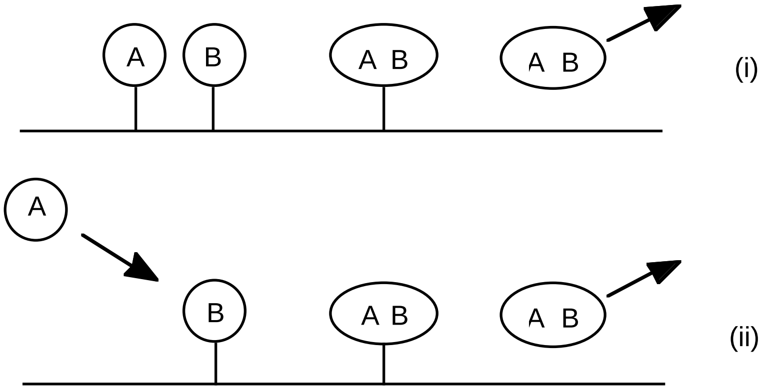

Fig. 2. Diagram of the Langmuir-Hinshelwood and the Eley-Rideal reaction mechanisms.

Radiation-Induced Reaction of Hydrogen and Oxygen in the Gas Phase and the Effect of Nitrogen.

Radical chain reactions form the basis of the H_2/O_2 recombination process in the gas phase[18]. The most important of these reactions are:

$H_2 + O_2 = 2OH$ chain initiation

$OH + H_2 = H_2O + H$ chain propagation

$H + O_2 = O + OH$ chain branching

$O + H_2 = H + OH$ chain branching

$H + = \frac{1}{2}H_2$ chain termination

$H + O_2 + M = HO_2 + M$ chain termination

where M is any third body that promotes the combination of H and O_2.

Radiation generates ions, excited molecules, and radicals in the gas phase. The energy of such species is far more than sufficient to initiate chain recombination reactions of H_2 and O_2. Accordingly, the G values for the recombination of gaseous hydrogen and oxygen have been reported to range from about 10 to several hundred, depending on temperature, pressure, and other conditions[19].

The first reported studies of the radiation-stimulated recombination of hydrogen and oxygen were conducted using radon alpha particles[21]. Although these studies involved “clean” systems of the reacting gases (and the presumably inert gas radon), equilibrium amounts of mercury vapor (from displacement equipment and/or diffusion pumps) were likely present. The reported data allow the calculation of $G(H_2O) = G(-H_2) = \sim 10.2$. Dautzenberg reported similar results[22] and noted that the G-values are dependent upon conditions. Lind also reported measurements as a function of temperature that indicate that even higher G values are attained at higher temperatures.[19]

Haschke, et al. reported hydrogen/oxygen recombination over pure PuO_2 in a single experiment[2]. Rapid reaction of H_2 and O_2 was observed. Recent work by Morales, with both pure and impure PuO_2 confirmed this result[3]. Both reports concluded that catalytic rather than radiolytic effects dominate under their experimental conditions. However, it appears that the data also can be modelled radiolytically and appear to be consistent with the literature reports discussed above. [22]

Dautzenberg[20,21] performed an extensive series of studies of the radiation-induced reaction of gaseous hydrogen and oxygen. He reported very high G-values for the recombination reaction, exceeding 100 under certain conditions, indicative of chain reactions. His results showed that the presence of nitrogen gas greatly increases the rate of reaction and that increasing temperature leads to increasing G-values. Dautzenberg interpreted the complex results in terms of a chain reaction, with chain propagation likely involving the radical HO_2. His results also indicate the significance of surface reactions in determining the reaction chain length.

Kalashnikov et al.[23] also reported that under certain conditions of gas pressure and composition, long chain lengths can be attained with $G(H_2O)$ exceeding 100, confirming very high radiolytic G-values for the hydrogen/oxygen reaction. Therefore, it does not appear credible that significant pressures of hydrogen and oxygen can co-exist in the presence of strong ionizing source because recombination rates will greatly exceed radiolytic decomposition rates of water.

Dautzenberg's work ignored reactions that consume nitrogen and considered it an inert gas. However, in radiolytic systems with an initially high proportion of air, as occurs often in plutonium storage environments, the literature indicates that radiation-induced reactions between oxygen and nitrogen also will occur relatively rapidly. These reactions have been shown to produce nitrogen oxides[21] and, if water is present, nitric acid[23]. It also is well known that nitric acid can react with oxide or metal surfaces to form solid nitrates. As mentioned earlier, nitrates dissolved in liquid water retard the radiolytic formation of hydrogen. Therefore, a contributing factor to the generally observed disappearance of oxygen from air-sealed Pu storage containers during storage may be formation of surface-adsorbed nitric acid or nitrate. The G values for nitrogen/oxygen reactions, while significant, are lower than G values for the hydrogen/oxygen reaction.

Radiolysis of a nitrogen-hydrogen-oxygen mixture is reputed to be extremely complex, apparently involving more than two hundred reactions.[19, 23,24, 25] The production of nitric acid from moist air is reported to proceed with a G (nitric acid) of 2.0.

Conclusions

1. The H_2/O_2 recombination reaction in the absence of ionizing radiation has been studied intensely. Surface catalytic effects can dominate under some circumstances, including plutonium storage environments.

2. Radiolytically-induced recombination of hydrogen and oxygen can be highly efficient via chain reaction ($G>100$). The recombination rate is strongly affected by surfaces and to some extent by the presence of other gases, such as nitrogen. Radiolytic reactions of nitrogen can lead to adsorbed nitrates.

3. The literature indicates that G values for radiolytic decomposition of adsorbed water are strongly dependent upon the nature of the sorbent material. G values much greater and much lower than for liquid water are observed, depending upon the surface.

4. Rapid hydrogen/oxygen recombination occurs over PuO_2, providing a strong technical basis that hydrogen and oxygen cannot co-exist at significant pressures in plutonium storage environments.

Acknowledgements

This work was supported by the EM66 Nuclear Materials Stabilization Program Office, United States Department of Energy, Albuquerque Operations and Headquarters Offices, under the auspices of the DNFSB 94-1 Research and Development Project.

References

1. “Criteria for Preparing and Packaging Plutonium Metals and Oxides for Long-Term Storage,” U. S. Department of Energy Standard DOE-STD-3013-96, September 1996.

2. Haschke, J. M., Allen, T. H., Stakebake, J. L., “Reaction Kinetics of Plutonium with Oxygen, Water and Humid Air: Moisture Enhancement of the Corrosion Rate”, *Journal of Alloys and Compounds* **243** (1996) 23. (b) Haschke, J. M. and Ricketts, T. E., “Plutonium Dioxide Storage: Conditions for Preparation and Handling”, Los Alamos National Laboratory report LA-12999-MS, August 1995. (c) Haschke, J. M. and Martz, J. C., chapter titled “Plutonium Storage”, *Encyclopedia of Environmental Analysis and Remediation*. Robert A. Meyer ed. John Wiley and Sons, Inc, New York City, 1998.

3. Morales, L., “Preliminary Report on the Recombination Rates of Hydrogen and Oxygen over Pure and Impure Pu Oxides”, Los Alamos National Laboratory report LA-UR-98-5200, January 1999.

4. Haschke, J.M. and Ricketts, T. E. “Adsorption of Water on Plutonium Dioxide”, *J. Alloys and Compounds*, **252** (1997) 148.

5. Quigley, G.P., “Hydrogen/Oxygen Recombination Rates in 3013-Type Environments: An Interim Report on the Rate of Loss of Hydrogen in Dry Air from Cell Containing Non-Radiolytic Samples”, Los Alamos National Laboratory report LA-UR-98-4864. January, 1999.

6. DNFSB Recommendation 94-1 Research and Development Program, Material Identification and Surveillance Project. See Los Alamos National Laboratory report LA-UR-98-2005 “Materials Identification and Surveillance Project Item Evaluation Item: Rocky Flats Plutonium Oxide Sample 011589.”

7. Bugaenko L. T. Byakov V. M. and Kabakchi S. A. “Mechanism of the Radiolysis of Water”, *High Energy Chemistry*, **19** (1985) 233.

8. Bibler: N. E. Bibler, “Curium-244 α Radiolysis of Nitric Acid. Oxygen Production from Direct Radiolysis of Nitrate Ions”, *J. Phys. Chem* **78** (1974) 211.

9. Spinks, J. W. T. and Woods, R. J., *An Introduction to Radiation Chemistry, 2nd Ed.*, Wiley, New York City, 1976.

10. Aleksandrov, A. B., A. Yu. Bychkov, A. I. Vall, N. G. Petrik, and V. M. Sodov, “Radiolysis of Adsorbed Substances on Oxide Surfaces”, *Russ. J. Phys. Chem.* **65** (6) (1991) 847-849.

11. (a)Garibov, A. A., M. M. Melikzade, M. Y. Bakirov, and M. Kh. Ramazonova, “Radiolysis of Adsorbed Water Molecules on the Oxides Al_2O_3, La_2O_3, Er_2O_3, and BeO”, *High Energy Chem.* **16** (1982), 177-179. (b) Aleksandrov, A. B., A. Yu. Bychkov, A. I. Vall, N. G. Petrik, and V. M. Sodov, “Radiolysis of Adsorbed Substances on Oxide Surfaces”, *Russ. J. Phys. Chem.* **65** (6), (1991) 847-849.

12. (a) Oak Ridge National Laboratory, “Chemical Technology Division Annual Progress Report for Period Ending May 31, 1965”, ORNL-3830, pp. 233-235.(b) Oak Ridge National Laboratory, “Chemical Technology Division Annual Progress Report for Period Ending May 31, 1966”, ORNL-3945, pp. 218-220.

13. Garibov, A. A., V. N. Parmon, T. N. Agaev, and R. D. Kasumov, “Influence of the Polymorphous Forms of the Oxide and the Temperature on the Transfer of Energy During Radiation-Induced Heterogeneous Processes in the $Al_2O_3 + H_2O$ System”, *High Energy Chemistry* **25, 86** (1991).

14. Lewis, B. and G. von Elbe *Combustion Flames and Explosions of Gases*, 3rd Edition, Academic Presss, Inc., 1987. This book provides the scientific basis for understanding combustion, Chapter 1 gives a good introduction and Chapter 2 deals with the reaction between hydrogen and oxygen.

15. Coward, H. F. and G. W. Jones “ Limits Flammability of Gases and Vapors”, Bulletin 503, United States Bureau of Mines, 1952.

16. Smith, W. V., “The Surface Recombination of H atoms and OH Radicals”, *J. Chem. Phys*. **11** (1943).

17. Weinberg, W. H., “Eley-Rideal Surface Chemistry: Direct Reactivity of Gas Phase Atomic Hydrogen with Adsorbed Species”, *Acc. Chem. Res*. **29** (1996) 479. This review uses four specific examples to illustrate the important concepts of the Eley-Ridel surface chemistry mechanism.

18. Warnatz, J., U. Maas, and R. W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. Springer-Verlag Berlin Heidelberg, 1996. This book provides a basic background on combustion, with sections on radical chain and surface reactions.

19. Lind, S. C., *Radiation Chemistry of Gases*, Reinhold, New York City, 1961.

20. Dautzenberg, D., "Gamma-Radiolysis of Hydrogen-Oxygen Mixtures—Part I. Influences of Temperature, Vessel Wall, Pressure and Added Gases (N_2, Ar, H_2) on the Reactivity of H_2/O_2 Mixtures", *Radiat. Phys. Chem.* **33** (1), (1989) 61.

21. Dautzenberg, D., "Gamma-Radiolysis of Hydrogen-Oxygen Mixtures—II. Influence of the Additives H_2O, HNO_3, CO_2, Ethanol, n-Pentane and NO_2 on the Reactivity of H_2-O_2-N_2 Mixtures", *Radiat. Phys. Chem.* **36** (6) (1990) 767-70.

22. Hyder, L., unpublished results.

23. Kalashnikov, N. A., B. S. Kalinichenko, V. G. Kulazhko, and I. K. Shvetsov, "Experimental Study of the Alpha Radiolysis of Water Vapor", *Sov. At. Energy* **69** (1990) 567-71. (b) Reed, D. T. and R. A. van Konynenberg, "Effect of Ionizing Radiation on Moist Air Systems", *Proc. Matl. Res. Soc. Symp.* **112** (1988) 393-404.

24. May, R., D. Stinchcombe, and H. P. White, "The Radiolytic Formation of Nitric Acid in Argon/Air/Water Systems", AERE R8176, Harwell, UK, January, 1992.

25. Henshaw, J., "Modelling of Nitric Acid Production in the Advanced Cold Process Canister Due to Irradiation of Moist Air", SKB-94-15, Swedish Nuclear Fuel and Waste Management Co., Stockholm, January, 1994.

Additional Topical References to Hydrogen/Oxygen Reactions

Texts

I. Glassman. *Combustion* 3rd ed. Academic Press, San Diego CA, 1996. This text is another good general reference on combustion. Detailed specific reaction rate constants are provided for the H_2/O_2 mechanism.

Anderson, A. E., “Inorganic Gases”, in *Fundamental Processes in Radiation Chemistry*, P. Ausloos, Ed., Interscience, New York City, 1968.

Interaction of H_2 with Stainless Steel

Moore, B. C., “Recombination Limited Outgassing of Stainless Steel”, *J. Vac. Sci. Technol.* A **13** (1985) 545.

Horgan, M., and I. Dalins. “Adsorption Of Hydrogen, Carbon Monoxide And Oxygen On Vacuum Degassed Stainless Steel 304 At 20 Deg”, *J. Vac. Sci. Technol.* **10** (1973) 559.

Holland, L., W. Steckelmacher, and J. Yarwood, Eds. *Vacuum Manual.* Wiley and Sons, New York, 1974.

Gas Phase Reactions

Reed, D. T. and R. A. van Konynenberg, “Effect of Ionizing Radiation on Moist Air Systems”, *Proc. Matl. Res. Soc. Symp*. **112** (1988) 393-404.

Kalashnikov, N. A., B. S. Kalinichenko, V. G. Kulazhko, and I. K. Shvetsov, “Experimental Study of the Alpha Radiolysis of Water Vapor”, *Sov. At. Energy* **69** (1990) 567-71.

Wright, J., J. K. Linacre, W. R. March, and T. H. Bates, “Effect of Radiation on Heterogeneous Systems of Air or Nitrogen and Water”, *Proceedings of the 1955 Geneva Conference on the Peaceful Uses of Atomic Energy* **17** (1955) 560.

Howson, A. and R. Simmons “The Kinetics Of The Thermal Reaction Between Hydrogen And Oxygen In Barium Bromide-Coated Reaction Vessels”, *Symp. Combust.* **11** (1966) 1081.

Westbrook, C. K. and F. L. Dryer. “Chemical Kinetic Modeling of Hydrocarbon Combustion”, *Prog. Energy Combust. Sci.* **10** (1987) 1.

McKay. G., “The Gas-Phase Oxidation of Hydrocarbons”, *Prog. Energy Combust. Sci.* **3** (1977) 105.

Gardomer, W. C. and D. B. Olson. “Chemical Kinetics of High Temperature Combustion”, *Ann. Rev. Phys. Chem.* **31** (1980) 377.

Dimitrov, V. I., N. A. Golubkova, and Y. Korobeinikov. “Calculation of Recombination Rate Constants in (H_2-O_2) System”, *React. Kinet. Catal. Lett.* **11** (1979) 319.

Bennett , J. E. and D. R. Blackmore. “Gas-Phase Recomination Rates of Hydrogen and Deuterium Atoms”, *J. Chem. Phys.* **53** (1970) 4400.

Blint, R. J., “Calculation of the rate constant for the reaction of atomic hydrogen with molecular oxygen to from the free radical HO_2”, *J. Chem. Phys*. **73** (1980) 765.

Yamawaki, M. K. Yamaguchi, S. Tanaka, T. Namba, T. Kiyoski, and Y. Takahashi, “Effect of Surface Impurities on the Hydrogen Recombination Coefficient of First-Wall Materials”, *J. Nucl. Mat.* **162** (1989) 1071.

Henrie, J. O., “The Effects Of Hydrogen Generation On Radioactive Waste Handling Technology”, *Nuclear Technology* **87** (1989) 729.

Hinshaw, J., “Modeling of Nitric Acid Production in the Advanced Cold Process Canister Due to Irradiation of Moist Air”, SKB Tech. Report 94-15 (1994).

Arkhipov, O. P., V. L. Bugaenko, V. K. Dushin, A. I. Zabeida, S. A. Kabakchi, V. T. Kireev, and E. I. Ruzavin, “Radiolytic Hydrogen Formation and Evaluation of Explosion Parameters for Hydrogen-Steam-Oxygen-Nitrogen Mixtures in Primary Circuit Units of a VVER-1000 Nuclear Reactor”, *High Energy Chem.* **28** (5), (1994) 341-8.

Nishimura, K. and N. Suzuki, “Radiation Treatment of Exhaust Gases, XIII. NH_3 Consumption in Moist NO-SO_2-O_2-N_2 Mixtures Containing NH_3, *J. Nucl. Sci. Technol.* **18** (5) (1981) 341-8.

Nishimura, K. and N. Suzuki, “Radiation Treatment of Exhaust Gases, XIV. Analysis of NO Oxidation and Decomposition in Dry and Moist NO-O_2-N_2 Mixtures by Computer Simulation”, *J. Nucl. Sci. Technol.***18** (11) (1981) 878-86.

Etoh, Y., H. Karasawa, E. Ibe, M. Sakagami, and T. Yasuda, “Radiolysis of N_2-H_2O Systems”, *J. Nucl. Sci. Technol***.** **24** (8) (1987) 672-4.

Shvedchikov, P., E. V. Belousova, B. G. Dzantiev, S. U. Pavlova, and O. O. Sirotyuk, "Electron-Beam Radiolysis of NO_x-N_2-O_2-H_2O Mixtures", *Proc. Tinahy Symp. Radiat. Chem.* **6** (2) (1987) 729-34.

Shvedchikov, P., E. V. Belousova, S. U. Pavlova, B. G. Dzantiev, and O. O. Sirotyuk, "Thermal and Radiation-induced Thermal Oxidation of Nitric Oxide in NO_x-N_2-O_2-H_2O Mixtures at 25 – 280 °C", *High Energy Chem.***21** (5) (1987) 362-5.

May, R., D. Stinchcombe, and H. P. White, "The Radiolytic Formation of Nitric Acid in Argon/Air/Water Systems", AERE-R-8176 (Rev. 1), AEA Reactor Service, Harwell, U. K. (1992).

Heterogeneous Reactions of Adsorbed Moisture or Gases

Kammler, T., M. Scherl, and J. Kuppers. "Interaction of H atoms with oxygen adsorbed on Ni(100) surfaces: deirect reactions towards OH and H_2O", *Surf. Sci.* **382** (1997) 116.

Nieuwenhuys, B. E., "Adsorption and Reactions of CO, NO, H_2 and O_2 on group VIII metal surfaces", *Surf. Sci.* **126** (1983) 307.

Ponec, V., Z. Knor, and S. Cerny. *Chemisorption and interaction of hydrogen and oxygen on transition metals* Proceedings of the Third International Congress on Catalysis, Eds Sachtler, Schuit and Zwietering, North-Holland publishing company, Amsterdam, 1968.

Norton, P. R., in *The Chemical Physics Of Solid Surfaces And Heterogeneous Catalysis* King and Woodruff, Eds. Chapter 2: "The Hydrogen-Oxygen Reaction On Metal Surfaces", Elsevier, 1982. A good overview on the surface aspects of the reaction, with details on well defined surfaces.

Hoare, D. E., G. B. Peacock, and G. R. D. Ruxton. "Efficiency of Surface in Destroying Hydrogen Perxoide and Hydroperoxyl Radicals", *Trans. Faraday Soc.* **63** (1967) 2498.

Kharlamov, V. F. and Lisezky, "Kinetics of Heterogeneous Recombination of Hydrogen Atoms on Solid Surfaces", *React. Kinet. Catal. Lett.* **61** (1997) 123.

Garibov, A. A., Kh. G. Gezalov, G. Z. Velibekova, A. T. Khudiev, M. Kh. Ramazanova, R. D. Kasumov, T. N. Agaev, and A. M. Gasanov, "Influence of Water Concentration in Adsorbed Phase on Hydrogen Yield in Heterogeneous Water Radiolysis", *Khim. Vys. Energy* **21** (6) (1987) 505-10.

Garibov, A. A., G. Z. Velibekova, R. D. Kasumov, Kh. B. Gezalov, and T. N. Agaev, "Regularities in the Energy Transfer During Heterogeneous Radiolysis of Water in the Presence of Amorphous Aluminosilicate", *Khim. Vys. Energ.***24** (3) (1990) 204-209.

Rustamov, M. I., A. A. Garibov, A. M. Aleskerov, and R. D. Kasumov, "Kinetics of Paramagnetic Radiation Defects Growth in Zeolite-Containing Catalyst Zeokar-2", *Khim. Vys. Energ*. **23** (5) (1989) 471-2.

Nakashima, M. and Y. Aratono, "Radiolytic Hydrogen Gas Formation from Water Adsorbed on Type A Zeolites", *Radiat. Phys. Chem.* **41** (3) (1993) 461-5.

Aoki, M., C. Nakazato, and T. Masuda, "Hydrogen Formation from Water Adsorbed on Zeolite During Gamma Irradiation", *Bull. Chem. Soc. Japan* **61** (6) (1988) 1899-1902.

Gezalov, A. A., G. M. Zhabrova, and O. V. Krylov, "Mechanism for the Radiation Chemisorption of Oxygen and Hydrogen on Zinc and Aluminum Oxides", *High Energy Chem.* **5** (2) (1971) 141-2.

Zhabrova, G. M. and A. A. Gezalov, "Chemisorption of Hydrogen and Oxygen on Zinc and Aluminum Oxides During the Action of Gamma-Radiation", *Probl. Kinet. Katal.* **14** (1970) 242-50.

Gezalov, A. A. and G. M. Zhabrova, "Study of the Chemisorption of Hydrogen and Oxygen on Zinc and Aluminum Oxides Under the Action of Gamma Radiation", *Kinet. Cata.* **8** (2) (1967) 397-400.

Dickson, L. W. and A. Singh, "A Review of Applications of Radiolysis in the Absorbed State", *Proc. Ann. Conf. – Can. Nucl. Soc***. 7** (1986) 76-9.