Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 17-18, 2018

Review of the Property Differences of Hydrogen and Deuterium for the Accident Consequences in CANDU Reactors

J. Y. Jung [a*], Y.M. Song[a], J.H. Bae [a], S.Nijhawan [b]
[a]*Thermal Hydraulics Severe Accident Research Division, KAERI, Daedeok-daero 989-111, Daejeon, Korea*
[b]*Prolet Inc., Toronto, Canada*
[*]*Corresponding author: agahee@kaeri.re.kr*

1. Introduction

The CANDU reactors are moderated and cooled by D_2O. Therefore, it is natural that any accidents resulting in unmitigated degradation in fuel cooling can only be expected to involve D_2O interactions with hot metals in degraded channel behavior and not H_2O interactions. However, for almost 40 years of safety assessments, only the easier to remember combustible gas isotope H_2 has been considered in production, detection and control. Even the Passive Autocatalytic Recombiners, developed over 20 years of research and great expense were only qualified and quantified for H_2 mitigation. Yet they are required to mitigate copious amounts of deuterium gases under certain accident conditions.

Safety assessments for Wolsong CANDU reactors started well before the reactor construction started in 1976 and have been updated periodically as per the licensing requirements set forward by various national regulatory agencies. While D_2O properties are considered in design and safety assessments, no safety report edition had addressed the question of D_2 vs. H_2 and no considerations have been put forward on any effects on risk assessments or in feedback to other predictions such as fission product releases and containment behavior. Many in the industry instinctively and per habit defensively claim that the two gases must have the same behaviour just because they are isotopes of the same element. Our research indicates that this is not correct and that there may be significant implications of the omission in considering the correct gas.

This paper compiles published information on deuterium gas properties and compares it to that for the lighter isotope of hydrogen. Differences in production rates by oxidation and other phenomena, such as radiolysis, energy release during these processes, transport phenomena, burns, flame acceleration, transition from burns to detonation and recombination rates are just some of the important aspects of the combustible gas phenomena that need to be reconsidered. Potential effect of a failure to consider D_2 in safety evaluations on various aspects of computations undertaken in support of risk assessments is discussed. Literature survey indicates that the differences in production, combustion and transport properties of the two gases are significant. Areas for further research are identified.

A 1948 paper [1] on properties of different isotopes of hydrogen is still a classic. It laid out reasons for always considering the proper equation of state and proper fluid properties. It demonstrated that deuterium and tritium differ from common hydrogen in a number of fundamental ways. Table 1 shows some basic properties of D_2 and H_2.

Table 1 Basic properties of D_2 and H_2

	Deuterium	**Hydrogen**
Molecular weight [g/mole]	4.028	2.014
Critical Point		
Temperature [^{0}C]	-234.81	-240.01
Pressure [bar}	16.653	12.964
Density [kg/m3]	69,797	31.263
Triple point		
Temperature [^{0}C]	-254.44	-259.19
Pressure [bar]	1.71E-01	7.70E-02
melting point [^{0}C]	-254.42	-259.2
Boiling point [^{0}C]	-504.26	-252.78
Bond Energy [kJ/mole]	443.6	436
Density at NTP [kg/m^3]	0.178	0.089
Thermal conductivity [w/m-k]	0.14	0.187
Viscosity [kg/m.s]	1.25E-05	8.42E-06

2. Discussion of Properties of hydrogen Isotopes

Reference 1 presents a fundamental equation of state for deuterium and discusses its properties from solid to gaseous states. It identifies three states of a deuterium molecule – Normal deuterium, Ortho-deuterium and Para-deuterium. Inspection of data reveals a number of differences with properties of normal hydrogen.

The following three main areas are of interest in this research issue as the safety implications are basically in ability to predict, detect and mitigate any undesirable production of D_2.

A. Comparisons of D_2 and H_2 Properties

- Physical properties
- Transport properties
- Thermodynamic properties
- Chemical properties
- Combustion Properties

- Recombination properties

B. Comparison of Zircaloy and steel oxidation in D_2 and H_2.

C. Evaluation of reactor systems designed for H_2 for D_2 service:

- Detection,
- Measurement and
- Control (ignition, recombination) methods

2.1 Physical Properties

Using classic kinetic theory and verifications against data, physical properties of both deuterium and hydrogen were reported in great detail and in tabular form in reference 3. It is a very comprehensive compilation of derived deuterium gas properties. During the development of CANDU severe accident analysis codes such as ISAAC or ROSHNI, empirical equations for deuterium and hydrogen properties have been created. Sample plots of the comparison of physical properties – density, specific heat, viscosity and thermal conductivity are given in Figs. 1 ~ 4.

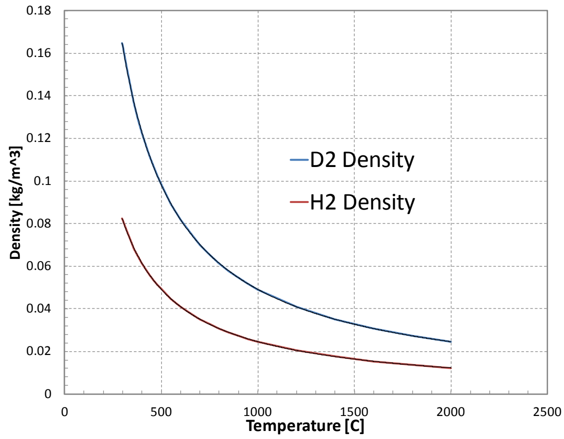

Fig. 1. D_2 and H_2 density at 1 atm

We have developed and documented empirical deuterium and hydrogen property correlations based on equations of state for use in severe accident codes.

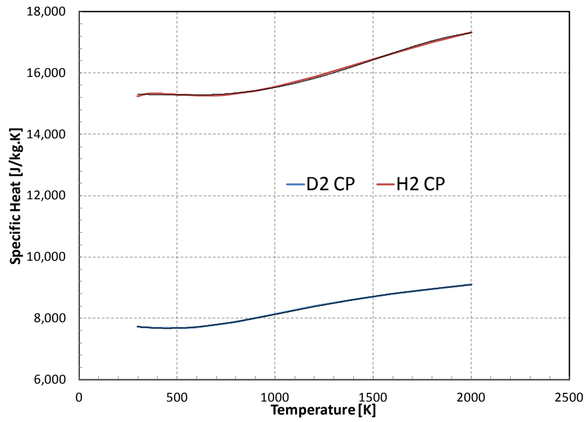

Fig. 2. D_2 and H_2 specific heat Cp at 1 atm

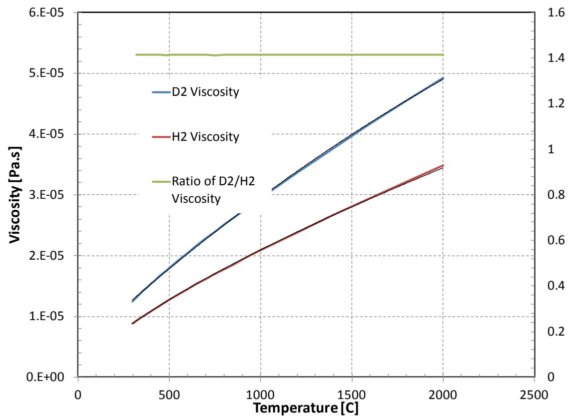

Fig. 3. D_2 and H_2 viscosity at 1 atm

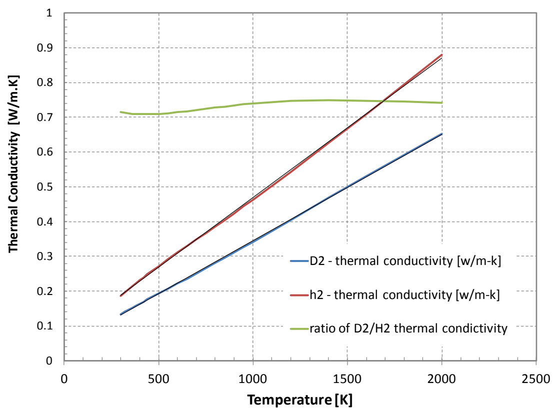

Fig. 4. D_2 and H_2 thermal conductivity at 1 atm

Diffusion coefficient ($\mu.C_p/k$) a derived transport property is illustrated in Fig. 5.

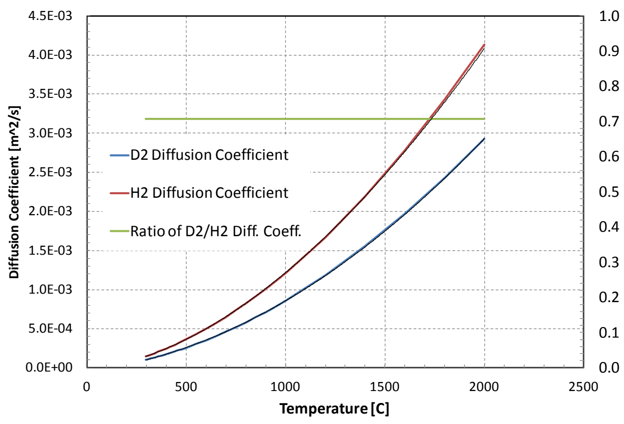

Fig. 5. D_2 and H_2 diffusion coefficient at 1 atm.

2.2 Chemical properties

In general deuterium has the same reactions as hydrogen. Deuterium Reaction rates are influenced by activation and bond energies which are greater for deuterium than for hydrogen. As a result deuterium reacts more slowly than hydrogen. That is also why deuterium is often used as a tracer in chemical and biochemical reactions involving hydrogen. It is also now being used as a bonding agent in medicines where higher bond energies are required in medical applications.
Reference 4 is an example of chemical reactions that have mild isotopic effect (5 to 10%) of hydrogen, deuterium and tritium.
Chemical reactions that are exothermic will release lower heat due to higher bond energy with deuterium. For Zircaloy reaction with steam the heat of reaction will be 7.3 kJ/mole less.

2.3 Combustion properties

A 1991 AECL paper by Grant Korrol and R.K. Kumar of AECL (reference 5) clearly enumerated differences between D_2 and H_2 in the basic combustion properties like flammability limits, laminar burning velocities and detonation cell widths. Information in this section is taken from that paper. It is interesting that AECL was aware of the differences between the two gases both in combustion and recombination but some unknown considerations inhibited work with or qualifiucations with deuterium which as significatnly different properties in combustion and recombination.
It was noted in reference 5 that deuterium combustion limits are higher both in upward and downward propogation of combustion flames. This confirmed a similar conclusion in reference 6 mentioned in reference 5.

Table 2 Flammability limits for D_2 and H_2 [5]

	Deuterium	**Hydrogen**
downward propagation limit [vol%]	**10.2**	**9**
Upward propagation limit [vol%]	**4.9**	**3.9**

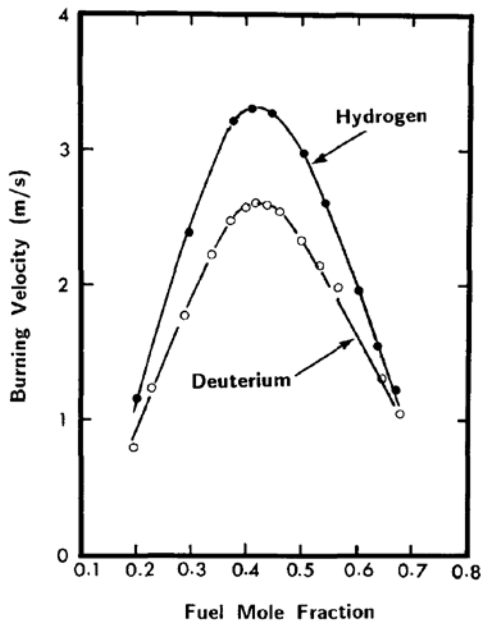

Fig. 6. Laminar burning velocities in air from D_2 and H_2 [5]

2.4 Recombination with Oxygen in air

Once the question of suitability of performance data for AECL wet proof catalysts for deuterium service was raised, a series of experiments were undertaken at Chalk river laboratories in Canada. Instrumentation issues and the small scale of the experiment not withstanding, significant differences (D_2 recombination upto 40% lower) in recombination capacity of these catalyst recombiners was orally reported at darlington licensing hearings in 2014. No published work exists and KAERI is investigating the issue further. It is important to note that in absence of sufficient recombination capacity, any deployed PARS would act as sources of ignition, flames and detonation.
Dissociation, absorption, diffusion, permeability and adsorption of gas X into a metallic surface Y strongly affect recombination of gas X with like molecules, with another gas or with itself on the metallic surface Y.
It was shown in reference 7 that recombination of deuterium atoms differes greatly from recombination of hydrogen atoms. This was explained using a semi-classical dynamic model of molecules and an Embedded Diatomics in Molecules potential.

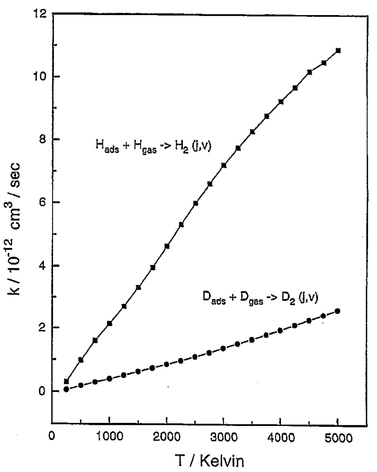

Fig. 7. Recombination rates of hydrogen and deuterium gases with like atoms on Cu [7]

Similar to the isotope dependence of hydrogen diffusion in crystalline materials, the kinetics of hydrogen absorption in the Pd-coated metallic glass was found to be twice faster than that of deuterium (reference 7, Fig. 8).

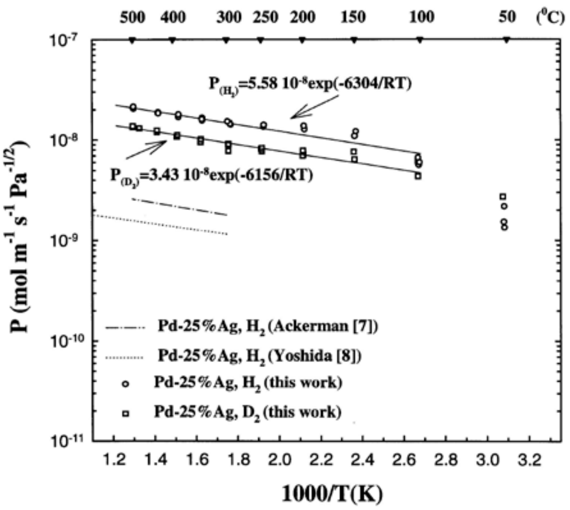

Fig. 8. Palladium permeability difference between D_2 and H_2 [8]

3. Discussion and implications on licensing safety assessments and severe core damage analyses

Differences in hydrogen and deuterium gas properties are significant enough to warrant an audit of implications of using H_2 data exclusively for detection, measurement and control of the two isotopes of hydrogen. A discussion of its implications should be documented.

4. Conclusions

Significant progress has been made in developing a data base of deuterium properties and deuterium behaviour in combustion and recombination. We have identified the issue of singularity of D_2 properties and the errors made in depending upon systems for H_2 detection, measurement and control at locations where H_2 may not exist. Further work is necessary in updating the safety reports and in updating station instrumentation calibration to reduce any residual risk.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT). (No. 2017M2A8A4017283).

References

[1] Compilation of Thermal Properties of Hydrogen in Its Various Isotopic and Ortho-Para Modifications, Harold W. Woolley, Russell B. Scott, and F. G. Brickwedde, US Department of Commerce, national bureau of Standards, research paper RP1932, Volume 41, November 1948.

[2] Fundamental Equation of State for Deuterium; Journal of Physical and Chemical Reference Data , Volume 43, 013103 (2014).

[3] Gaseous transport properties of hydrogen, deuterium and their binary mixtures from ab initio potential, Bo Song, Xiaopo Wang and Zingang Liu, Molecular Physics, Vol 111, No. 1, 49-59, 2013.

[4] Rates of Abstraction of Hydrogen, Deuterium and Tritium from Acetone in Alkaline Media, J.R. Jones, Trans. Faraday Soc., 1965, 61, 95 1964.

[5] Isotope Effects on the Combustion Properties of Deuterium and Hydrogen, G.W. Korrol and R.K. Kumar (Atomic Energy of Canada Limited), Combustion and Flame 84, pp 154-159, 1991.

[6] Hertzberg, M. Pittsburg Research center, PRC report 4305, 1981.

[7] Hydrogen and Deuterium recombination rates on copper surface, B.F. Hansen, G.D. Billing, Surface Science 373 (1997) L333-L338.

[8] Hydrogen and Deuterium in Pd-25 Pct Ag Alloy: Permeation, Diffusion, Solubilization, and Surface Reaction, E. Serra, M. Kemali, A. Perujo, And D.K. Ross, Metallurgical And Materials Transactions A Volume 29A, March 1998.