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The Hydriding Kinetics of Organic Hydrogen Getters

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Abstract

The aging of hermetically sealed systems is often accompanied by the gradual production of hydrogen gas that is a result of the decay of environmental gases and the degradation of organic materials. In particular, the oxygen, water, hydrogen "equilibrium" is affected by the removal of oxygen due to the oxidation of metals and organic materials. This shift of the above "equilibrium" towards the formation of hydrogen gas, particularly in crevices, may eventually reach an explosive level of hydrogen gas or degrade metals by hydriding them. The latter process is generally delayed until the oxidizing species are significantly reduced. Organic hydrogen getters introduced by Allied Signal Aerospace Company, Kansas City Division have proven to be a very effective means of preventing hydrogen gas accumulation in sealed containers. These getters are relatively unaffected by air and environmental gases. They can be packaged in a variety of ways to fit particular needs such as porous pellets, fine or coarse [gravel] powder, or loaded into silicone rubber. The hydrogen gettering reactions are extremely irreversible since the hydrogen gas is converted into an organic hydrocarbon.

These getters are based on the palladium-catalyzed hydrogenation of triple bonds to double and then single bonds in aromatic aryl compounds. DEB (1,4 bis (phenyl ethynyl) benzene) typically mixed with 25% by weight carbon with palladium (1% by weight of carbon) is one of the newest and best of these organic hydrogen getters. The reaction mechanisms are complex involving solid state reaction with a heterogeneous catalyst leading to the many intermediates, including mixed alkyl and aryl hydrocarbons with the possibilities of many isomers. The reaction kinetics mechanisms are also strongly influenced by the form in which they are packaged. For example, the hydriding rates for pellets and gravel have a strong dependence on reaction extent (i.e., DEB reduction) and a kinetic order in pressure of 0.76. Silicone rubber based DEB getters hydride at a much lower rate, have little dependence on reaction extent, have a higher kinetic order in pressure (0.87), and have a lower activation energy. The kinetics of the reaction as a function of hydrogen pressure, stoichiometry, and temperature for hydrogen and deuterium near ambient temperature (0° to 75°C) for pressures near or below 100 Pa over a wide range (in some cases, the complete) hydrogenation range are presented along with multi-dimensional rate models.

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Introduction

The aging of hermetically sealed systems is often accompanied by the gradual production of hydrogen gas that is a result of the decay of environmental gases and the degradation of organic materials. In particular, the oxygen, water, hydrogen “equilibrium” is affected by the removal of oxygen due to the oxidation of metals and organic materials. This shift of the above “equilibrium” towards the formation of hydrogen gas, particularly in crevices, may eventually reach an explosive level of hydrogen gas or degrade metals by hydriding them. The latter process is generally delayed until the oxidizing species are significantly reduced. Organic hydrogen getters introduced by Allied Signal Aerospace Company, Kansas City Division have proven to be a very effective means of preventing hydrogen gas accumulation in sealed containers. These getters are relatively unaffected by air and environmental gases. They can be packaged in a variety of ways to fit particular needs such as porous pellets, fine or coarse [gravel] powder, or loaded into silicone rubber. The hydrogen gettering reactions are extremely irreversible since the hydrogen gas is converted into an organic hydrocarbon.

These getters are based on the palladium catalyzed hydrogenation of triple bonds to single bonds in aromatic aryl compounds have been described by Balooch et al¹. DEB (1,4 bis (phenyl ethynyl) benzene) (A) mixed with 25% by weight catalyst (C-1% Pd) is one of the newest and best of these organic hydrogen getters. The reaction mechanisms are complex, involving solid state reaction with a heterogeneous catalyst leading to the many intermediates shown in Figure 1. Note that intermediates B and E have two isomers, cis and trans at the double bond, and that D has three isomeric forms, cis-cis, trans-trans, and cis-trans. There is,

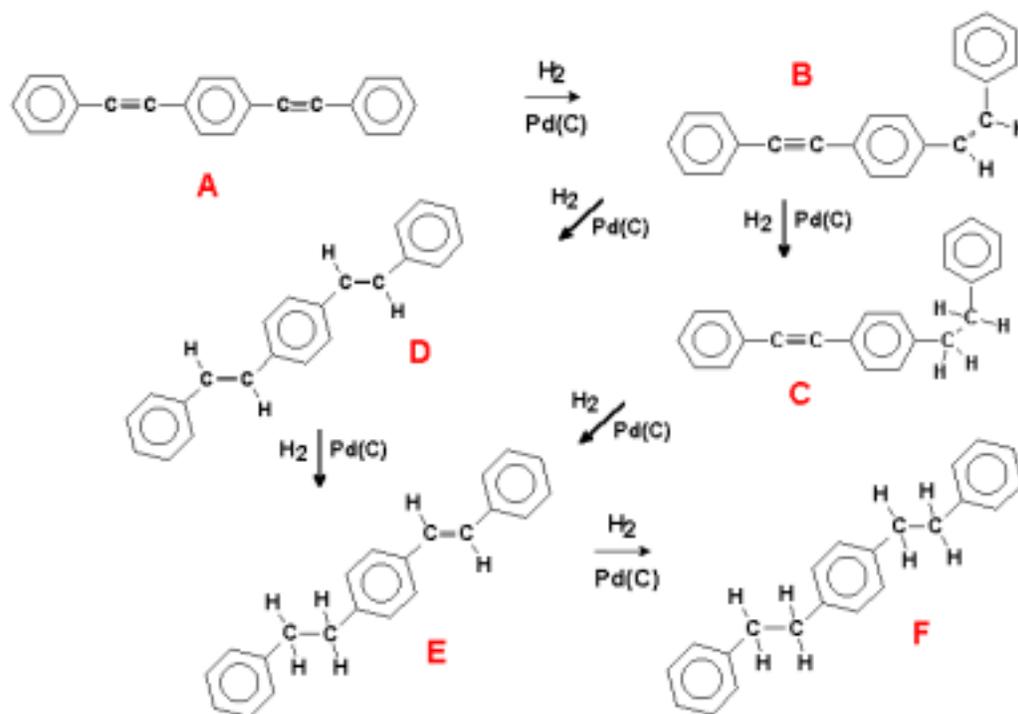


Figure 1: Reaction paths and intermediates in the palladium catalyzed hydrogenation of DEB.

however, little known of the kinetics of the reaction as a function of hydrogen pressure and stoichiometry of the hydrogenated organic species. The process becomes even more complex if deuterium is substituted for hydrogen as a means of tracing these mechanistic steps. This paper describes the measurement of the hydrogen and deuterium gettering rates of these materials at low pressures over the complete hydrogenation of the getter material.

Experimental

As a means of studying the rate of reaction of these getters, a gas buret system was chosen that consisted of a ~1-L volume having a pressure gauge (MKS 390AHA-00001, 1 Torr) serviced by an ultra-high-vacuum (UHV) system and an ultra-pure hydrogen, deuterium, and argon supply. This system was replicated four fold with all four systems serviced by the same vacuum system and gas supply. The hydrogen, deuterium (99.7% D), and argon were nominally Ultra High Purity Grade and with the hydrogen filtered through an UH_3 or UD_3 bed, respectively. The 1-L volumes and their valves (typically a Nupro H series with Cajon 4VCR fittings) were individually calibrated by weighing before and after filling them with water. They were attached to a smaller volume containing the pressure gauge, the vacuum port, and the sample chamber. These volumes were calibrated against the 1-L volume by argon expansion. The sample chamber (~30 mL) was attached to this 1-L volume to contain the getter material. The getter was reacted by gas expansion. The pressure drop of the reacting gas was monitored using a Nicolet 4094 digital oscilloscope with 15-bit precision and digital data storage. These gas buret techniques are similar to those previously applied to the study of the reactions of H_2 and D_2 with Pd and U^{2-7} .

Programs for the Nicolet oscilloscopes manipulated the data to yield the ideal gas law calculation of the moles of gas consumed from the pressure drop, and smoothed and differentiated these results to yield the rate of H consumption as a function of both time and pressure. These digital data were also transferred to a personal computer and converted to a spread sheet or text format taking the final form of four columns of text that included time, pressure, hydrogen (or getter) consumed, and rate of consumption. The pellet and gravel data processing took in all the sets of pressure drop data as a function of time for each sample, and did the ideal gas law calculations for a running balance of H and DEB consumption. A smoothing/differentiation/data-elimination routine reduced each data set from thousands of points to approximately 200 that span the range from 120 Pa to 0.1 Pa. For the silicone rubber "O-ring" specimen, the smoothing/differentiation/data-elimination process was done by fitting the logarithm of the pressure versus time data to a fifth-order polynomial using TableCurve2D (SSPS Science) software.

The experiments reported here used DEB getter in the form of 20-mg pellets (6-each, 120 mg), gravel (powder sieved -14/+40, 110 mg), and a silicone rubber "O-ring" (60% by weight silicone rubber, ~3-mm D, 3.111g, 0.00385 m^2). Measurements were made as a function of pressure (0.1 to 120 Pa), hydrogen isotope (H and D), and extent of reaction with the DEB (0 to 8 added H atoms per DEB molecule) at ambient temperature (nominally $20 \pm 2 \text{ }^\circ\text{C}$). These specimens of DEB were obtained from Allied Signal Kansas City Division and were 75% DEB and 25% catalyst (C-1%Pd). The fundamental system of units used were the moles hydrogen per grams getter, but was sometimes expressed as DEB hydrogenation stoichiometry. The system was sized such that 1 L of gas expanded onto 100 mg of DEB getter would convert ~5% of the getter, enough to yield small changes in the DEB stoichiometry for each experiment, yet allow complete conversion of the DEB in a finite number of experiments. The DEB conversion extent was accumulated from run to run.

Results

The results of a typical run for one gas buret expansion is shown in Figure 2 for the fourth expansion of deuterium onto DEB pellets (120 mg, 6 pellets). The pressure decay appears to be exponential, indicating a first order reaction rate. A closer look (amplified by the derivative) shows a fast rate component at early times and a less than perfect match of hydrogen conversion to an exponential rise.

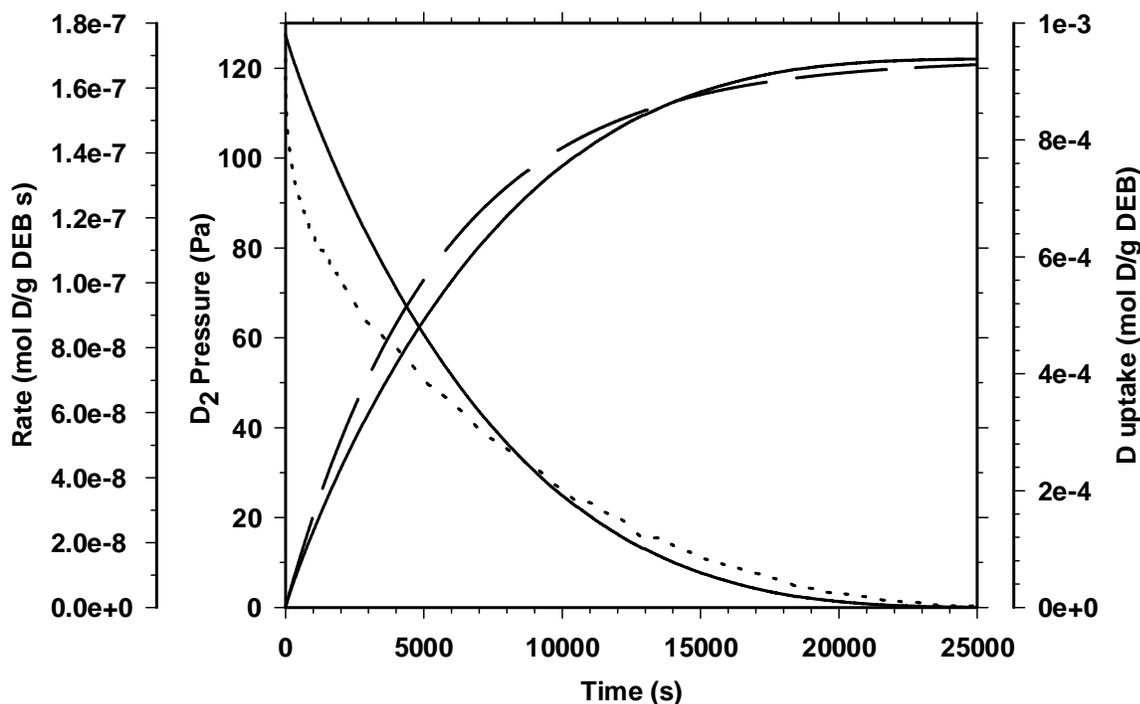


Figure 2: The fourth expansion of deuterium onto DEB pellets (120 mg, 6 pellets). Solid decay curve- D_2 pressure drop, Dashed rising curve-D uptake, Solid rising curve-simple exponential rise, Dotted curve-rate.

During early stages of hydrogenation of pellets and gravel, rate versus pressure for DEB hydrogen getter showed little effect of getter form or hydrogen isotope. As the experiment proceeded, the rate remained almost linear in pressure (~ 0.84 order) and decreased exponentially with DEB conversion. The fast component of the rate at early times persisted, but scaled as the overall rate. For pellets and gravel, hydrogen and deuterium, the initial rate spike was discarded by truncating all the data sets above 100 Pa. The remaining data are shown in Figures 3-6. The surface shown in Figs. 3-6 was generated using TableCurve-3D software fitting the data obtained at ambient temperature as the as the natural logarithm of rate (**Rate**, mol H (g DEB s) $^{-1}$) versus the natural logarithm of pressure (**P**, Pa), and the linear form of DEB reaction extent (**X**, mmol H (g DEB) $^{-1}$) to a somewhat planar surface. Equation 1 gives the model that to date gives the best description of the data.

$$\text{Rate} = A P^B [(De^{-EX} + e^{-CX})(1-X/F)/(D + 1)] \text{ (mol H g}^{-1} \text{ s}^{-1}) \quad (1)$$

The rate is expressed as a scaling factor **A**, the kinetic order for pressure **B**, and the term in square brackets for the decrease in rate due to the depletion of DEB involving two exponential processes (**C**, **D**, and **E**), and one stoichiometry limitation (**F** = 21.57 mmol H (g DEB) $^{-1}$). The fitting process found **A**, **B**, **C**, **D**, and **E**. The two exponential decay processes became apparent when a single exponential (i.e., **D** = 0) failed to adequately fit the high-pressure, low-consumption (i.e., the highest rate) part of the data. Fits using Eq. 1 to data of the form of Figs. 3-6 are given in Table I. The parameters in Table I were obtained by multiple curve fittings with some parameters being fixed within their error limits until most of the variability was dumped into parameter **A**. The parameters are not a unique set, but rather a simplified set that adequately represents the data.

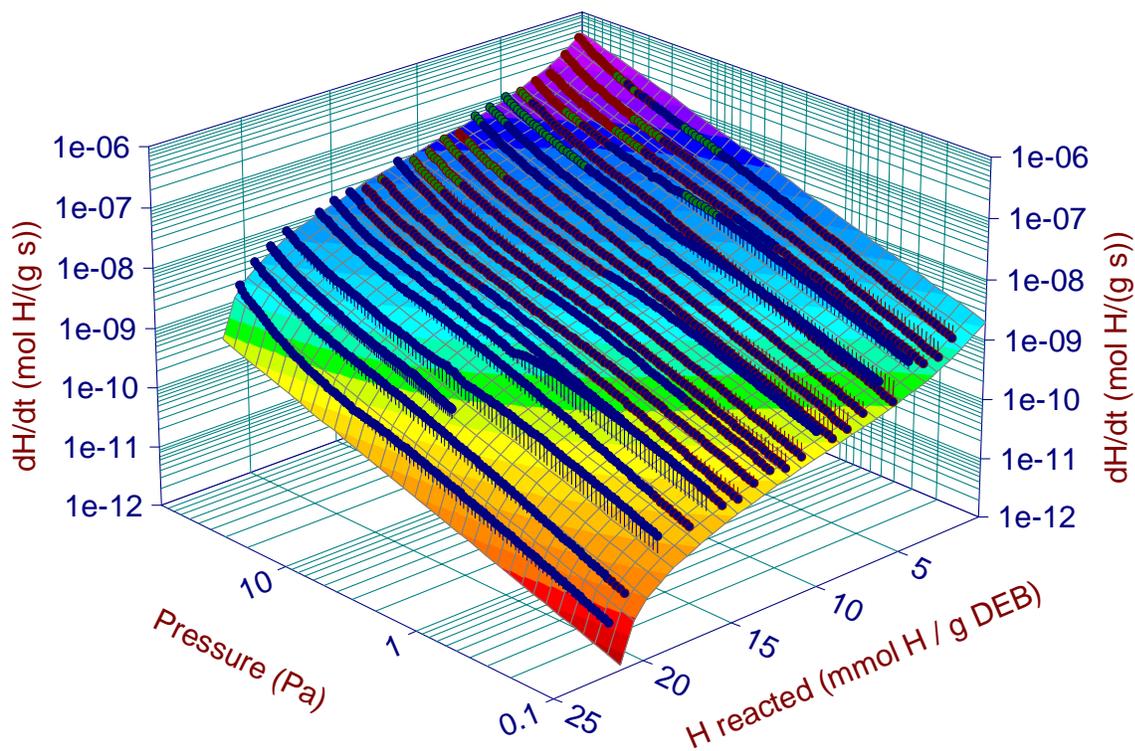


Figure 3: Hydriding rate of pellets as a function of pressure and reaction extent. Surface is described by Eq. 1 and parameters from Table I.

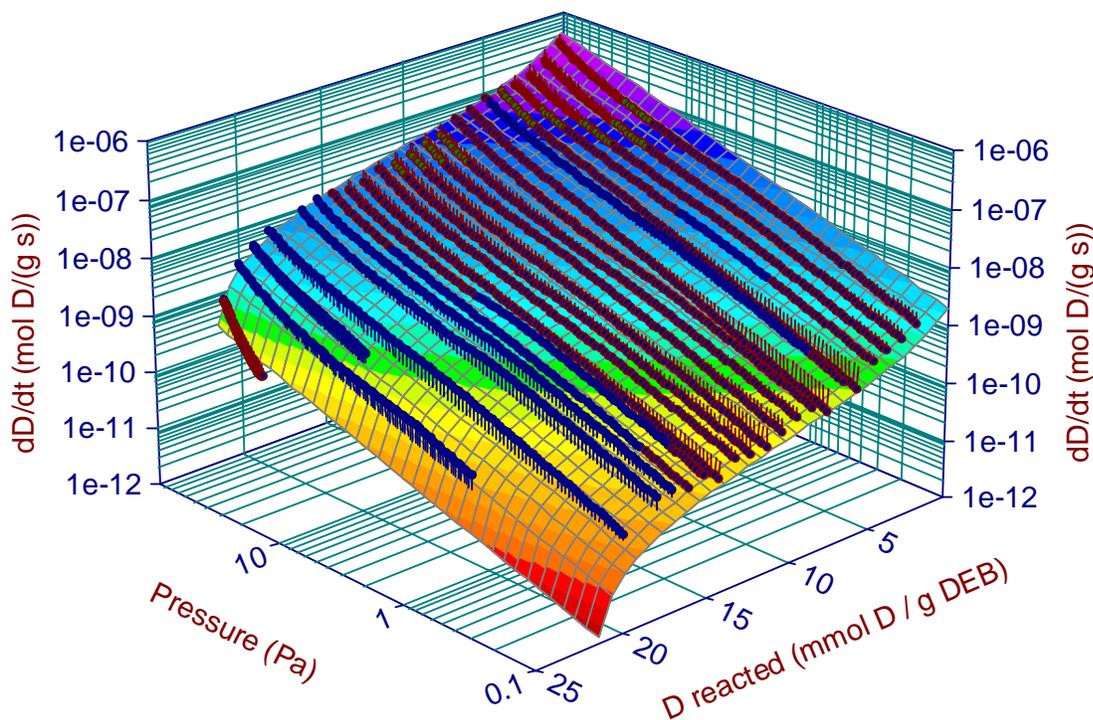


Figure 4: Deuteriding rate of pellets as a function of pressure and reaction extent. Surface is described by Eq. 1 and parameters from Table I.

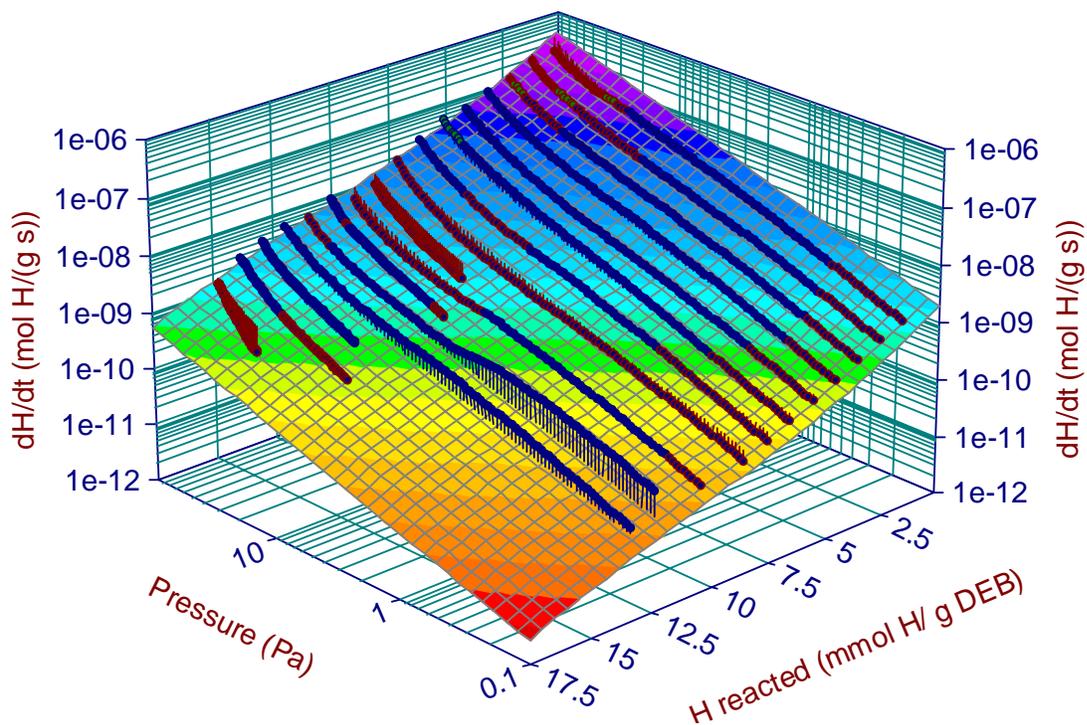


Figure 5: Hydriding rate of gravel as a function of pressure and reaction extent. Surface is described by Eq. 1 and parameters from Table I.

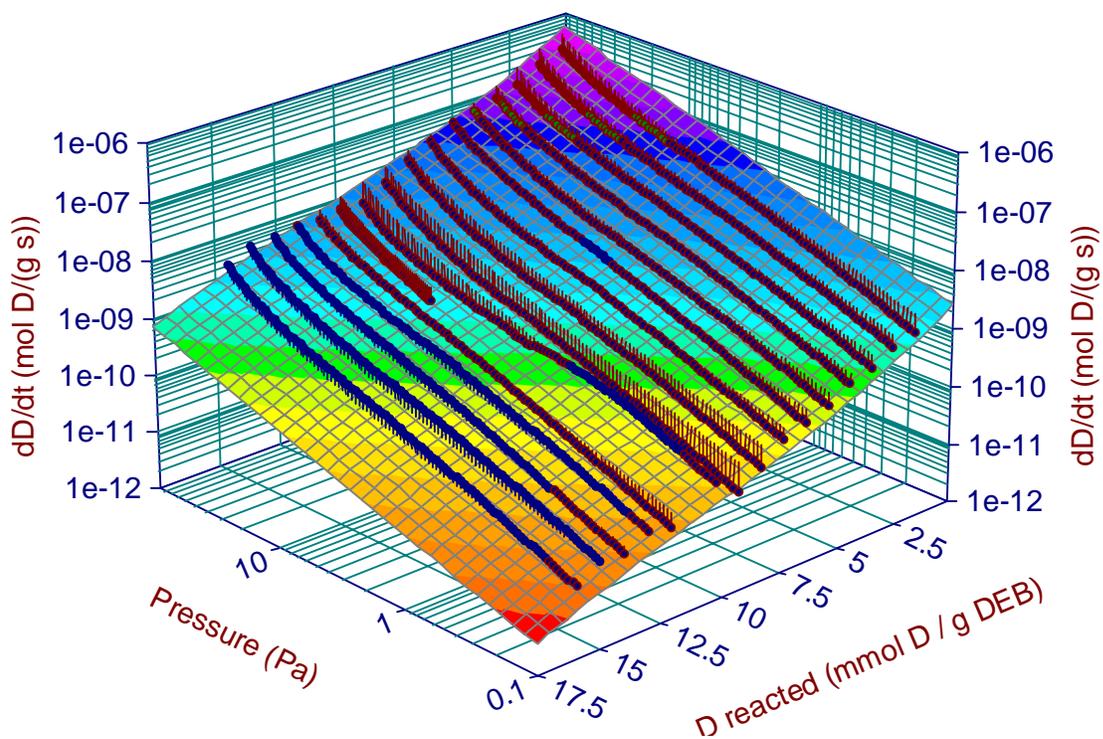


Figure 6: Deuteriding rate of gravel as a function of pressure and reaction extent. Surface is described by Eq. 1 and parameters from Table I.

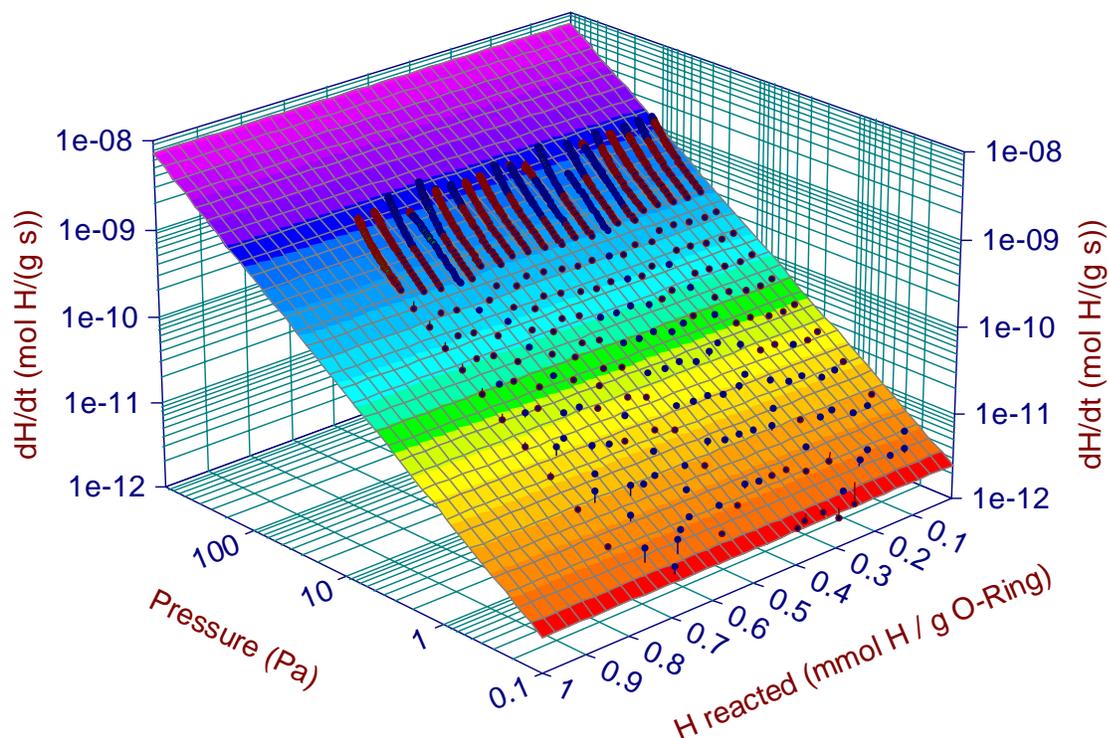


Figure 7: The hydriding rate of O-ring as a function of pressure and reaction extent. Surface is described by Eq. 2.

in close proximity to Pd atoms no longer are available. After that some migration of DEB is required for the reaction to proceed. As the pressure drops, the reaction slows, allowing more time for DEB migration to the Pd. Thus, the reaction speeds up relative to the pressure, which is the definition of a reaction of kinetic order less than one. As consumption of DEB proceeds, the reacting DEB must migrate through reduction products to bring the unsaturated bonds into contact with Pd.

The mechanism of the hydriding of the silicone rubber loaded specimen is very different from pellets and gravel. The gross reaction rate is less by a factor of ~ 500 when compared to previously unreacted pellets or gravel. The fact that a measurable rate was found was due to the fact that the O-ring specimen contained 10 times the amount of DEB used for the pellets and gravel. The kinetic order of the reaction in pressure is also less than that observed for the pellets and gravel. The reaction mechanism must regulate the accessible area of the specimen to a constant value in order to have a rate independent of consumption. Equation 1 for unreacted DEB pellets gives a hydriding rate of $9 \text{ E-}08 \text{ molH (g DEB s)}^{-1}$ compared to a value of $4.4 \text{ E-}07 \text{ molH (g DEB s)}^{-1}$ obtained from the results of Balooch et al.¹ for fine powders used in their experiments. The reaction rate of these DEB getter forms apparently has a very strong dependence on the particular form of the getter, and perhaps on the processing conditions for a particular form of getter.

Acknowledgements

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