



Research Article

Inhibition of LENR by Hydrogen within Gas-loaded Systems

Dennis Cravens*

P.O. Box 1317, Cloudcroft, New Mexico, USA

Abstract

This paper develops a model of reaction kinetics for Low-energy Nuclear Reactions (LENR) for gas loaded systems. The method is patterned after mathematics used in Michaelis–Menten kinetic models, which are standard in enzyme catalytic studies. Hydrogen is found to inhibit the deuterium reaction rates and can be explained by mixed inhibition kinetics where the hydrogen both competes with deuterium at the active sites requiring higher concentrations of deuterium for a given reaction rate and it also undergoes non-competitive inhibition, which alters the maximum rate of the reaction. This kinetic model predicts that hydrogen contamination would require higher loading ratios for similar reaction rates or heat production and also such contamination may lower ultimate heat production due to hydrogen active site complex productions.

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1. Introduction

A large number of mechanisms have been put forth in the field of Low-energy Nuclear Reactions (LENR). Most of these have addressed the difficulty of achieving the conditions of close range reactions between nuclear species and pathways. The high-level energy must leave the reaction sites without disrupting active sites. Here we will take a novel approach from the view of phenomenology and be interested only in the kinetics of the reaction and not the mechanism. The most common tools used in seeking to understand LENR have been nuclear and solid state studies. Here we will try to use biophysical methods to reveal some of the kinetics and material interactions played by the catalytic nature of the problem. It is hoped that this will give new methods for understanding this complex phenomenon.

The author will borrow heavily from the mathematics developed for enzyme catalysis. These methods are standard within biophysics but seem to be somewhat unknown outside the area. It seems clear that LENR proceeds primarily through some catalytic interaction between deuterium and some catalytic active host. In many ways its kinetics are similar to enzyme reactions where two substrate species have to seek out an enzyme, be accepted at an active site, react, and then release the product(s). The Michaelis–Menten kinetics developed within biophysics was developed to handle

*E-mail: Physics@tularosa.net

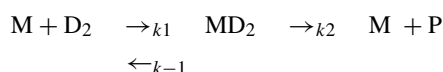
problems with these properties. This method dates back to 1913 [1] and was developed on the simple assumption that some reactions can proceed only when a catalyst and a substrate come in contact and their concentrations change slowly.

2. Kinetic Model and Mathematical Development

The kinetics of enzyme systems is well treated in most enzyme and biophysics texts [2]. We will adopt most of such mathematics directly but our terminology will be different since the product of concern here is heat, and we will be using inorganic active sites instead of enzymes, and nuclear species instead of substrates. Since many of our readers will be unacquainted with enzyme studies, we will use the simplistic “lock and key” analogy to help clarify by analogy. The catalytic agent is the “lock” and the reacting agent is the “key” in this analogy. The two have to connect correctly at the same place and time for there to be a reaction.

For the LENR events to proceed by a process similar to Michaelis–Menten kinetics we assume that (1) once the reaction occurs it is irreversible, (2) the reaction takes place quickly with few or no intermediate steps once correct conditions are present, (3) the reactions are rare enough that they do not significantly alter the deuterium concentration as the reactions proceed, and (4) the reactions do not appreciably alter the number of active sites. These are equivalent to the assumptions used in the standard Michaelis–Menten kinetics.

We will be addressing only the reactions within the host lattice and not the loading at the surface. It should be kept in mind that a more realistic treatment can be produced if the model were to be expanded to treat the loading process. Here we will only be considering processes that occur after loading of the sample. The kinetic reaction becomes:



Where M denotes the active site on or within the metal host, D₂ denotes deuterium (either entering as a D₂ molecule or in two events from separate D's), MD₂ denotes the deuterium active host complex, and P the product (here heat and any “nuclear ash”). k_1 denotes the forward reaction rate and k_{-1} the reverse reaction rate for forming the deuterium/host complex. k_2 denotes the forward reaction rate for the production of the products. Notice there is no reverse reaction rate expected for the high-energy reaction of LENR. That is to say the large energy release by the reaction prevents back reactions from the nuclear ash returning to deuterium species.

For this series of experiments we will be interested in the rate of production of the heat, which is our primary product. Our experimental variable will be the concentration of our reactant, D₂ and later the concentration of our inhibitor H₂. The well known result for the rate of product production for such kinetics is:

$$d[\text{P}]/dt = V_0 = k_2[\text{MD}_2] = k_2[\text{M}][\text{D}_2]/(K_m + [\text{D}_2]) = V_{\max}[\text{D}_2]/(K_m + [\text{D}_2])$$

or in the Lineweaver–Burk linear form for plotting,

$$1/V_0 = K_m/(V_{\max}^*[\text{D}_2]) + 1/V_{\max}.$$

For the value of

$$K_m = (k_{-1} + k_2)/k_1.$$

The value of $d[\text{P}]/dt = V_0$ represents the production rate of heat and nuclear ash. We did not attempt to measure the nuclear ash but could easily record the temperature differential in our experiments. The value of $V_{\max}$ is the maximum rate that can be expected if all our active sites are saturated with deuterium and nothing else alters them nor competes with deuterium to occupy the active regions. This would yield our highest possible heat production rate if we had no inhibition of the active sites, the deuterium availability was not limited, and the products could leave without disruption of the process. This would predict that the reciprocal of the heat production in our LENR system is expected to obey a

hyperbolic curve in regards to concentration of deuterium present at our active sites, and that we can expect large changes from changes in the deuterium concentrations for lower “loading ratios” and then smaller changes due to alterations in the concentrations past the $[D_2] = K_m$ value. The high slope and the rapid change of reaction rate to a plateau value indicate that K_m must be relatively small and hence: $K_1 > K_2$. That is to say that the binding of the deuterium to the active site is much easier than the progression to the production of heat via any possible nuclear channels. This is consistent with most LENR results. That is to say, the chemical binding is easy but the nuclear reactions more difficult, and the reaction is more predominant above some minimum concentration of deuterium [3].

However, most LENR systems are not as clean and simple as this. Hydrogen is a common contaminate, is very hard to remove from the experiments, will compete with deuterium for the active sites, alter the active sites so the deuterium cannot be bound, and may even bind to the deuterium active site complex in such a way as to prevent reactions from proceeding to completion.

Such conditions are common considerations in enzyme and catalytic systems. When this is admitted into the mathematics, the Michaelis–Menten kinetics must be modified. When an inhibitor competes directly with the reactant for the active site, the standard approach is called competitive inhibition. Then the modified production rate must be altered to:

$$V_i = V_{\max}[D_2]/\{K_m(1 + [I]/K_i) + [D_2]\}.$$

Notice that the K_m is simply modified by the factor $(1 + [I]/K_i)$ where the $[I]$ is the concentration of the competitive agent and K_i is its complex dissociation constant. When there is no inhibitor, $[I]$ we recover our original kinetics. When its dissociation constant is non-zero, the modification can become significant. The formation enthalpies are -19.1 kJ/mol for palladium hydride and -17.3 kJ/mol for the deuteride at 298 K [4]. Thus, in our case the hydride from the active complex is more stable than deuterium by about 2 kJ/mol. This means that a small amount of hydrogen can significantly reduce the overall reaction rate since it could slowly replace deuterium at the active site as the more stable configuration. Once bound it is not likely to freely dissociate from the active complex. In practice, the contamination by hydrogen would be revealed by a requirement to have higher loading ratios before attaining similar heat production rates. In that case, we would expect some researchers to have difficulty in seeing significant heat production if hydrogen contamination occurred, and that some would experience no results unless very high-loading ratios were achieved. In our lock and key analogy, it would be equivalent to having many fake useless keys mixed with our good keys so that the time needed to unlock the locks increases. You could enhance your chances of finding a good key by simply adding more good keys to the mix even if you cannot remove the bad ones. In this case, higher deuterium loading should increase the production rate of heat up to some maximum that is set by the number of active sites (number of locks).

Where heat is our measure of rate of reaction, $1/V_0$ becomes described by the linear equation:

$$1/V_0 = \{K_m(1 + [I]/K_i)\}/(V_{\max}^*[D_2]) + 1/V_{\max}.$$

This is a “linear” form used in plotting such kinetics. In our case, this allows our model to form a complex with the active site with hydrogen that does not lead to the production of heat. The fundamental assumption in the derivation of such model is that there are some active sites that are occupied by hydrogen instead of deuterium that do not lead to the production of heat.

Non-competitive inhibition occurs when the inhibitor forms a complex containing both the reactant and the active site. In our case that would be equivalent to a D and H occurring at an active site and not being able to proceed to the production of heat. In enzyme systems such non-competitive inhibition signifies that the binding of the inhibitor at one area of catalyst creates a complex that prevents reactions to take place. This would seem to signal in our case that the presence of hydrogen would cause more tightly bound hydrogen–hydrogen or deuterium–hydrogen pairs at the active site that would prevent reactions. In our lock and key analogy, this is like having some bad keys getting stuck in some

of the locks. Your maximum production rate is dropped since some of the locks are taken out of commission for some of the time. Even if you add more good keys (deuterium) you will never recover your higher rates.

In that case, the constant $1/V_{\max}$ term also must be altered by the factor containing the concentration of the inhibitor, $1 + [I]/Ki$.

And the overall equation becomes:

$$1/V_0 = \{K_m(1 + [I]/Ki)\}/(V_{\max}^*[D_2]) + \{1 + [I]/Ki\}/V_{\max}.$$

For this work, we note that the rate of product production is proportional to our observed temperature differential,

$$d[P]/dt = V_0 \text{ or } 1/V_0 = a/\Delta T$$

and the concentration of the reactant is proportional to the deuterium partial pressure, P_d ,

$$[D_2] = b^*P_d.$$

The modification due to the inhibitor can be set to a constant for a set hydrogen partial pressure or concentration,

$$c = \{1 + [I]/Ki\}.$$

The values a , b , and c are constants chosen to allow easy unit conversion. The value of c is constant and set for specific experimental conditions since the value of Ki is not easily obtained directly. The overall equation then becomes:

$$a/\Delta T = (c^*K_m)/(V_{\max}^*b^*P_d) + c/V_{\max}.$$

This is our general expression for “mixed inhibition” at a set temperature and inhibitor concentration. It allows for both the inhibition by direct competition with hydrogen for the active site and the production of a hydrogen/deuterium/active site complex that would prevent or slow the reaction rates. If we are correct in our assumed kinetics, we should get a series of approximately linear Lineweaver–Burk plots, which have higher slopes and higher intercepts as the inhibitor concentration is increased.

3. Experimental

A series of experiments were run with a range of deuterium and hydrogen gas ratios and pressures. The material containing the active sites was produced by BCT partners and contains predominately Pd and Ni held within fine Y stabilized zirconium oxide proton conductive material with inclusions of ppm of rare earths, lanthanides and nickel. They use a proprietary method of production but it is generally described as production by underwater sparks in a reductive circulating solution of heavy water. The solution is further reduced with hydrazine, filtered (Millipore–0.22 μm) and the fines are recovered by vacuum distillation at 45°C. Five grams of the powder was placed in each small sheathed gas cylinder (typically used as CO₂ cartridges – Genuine Innovation – 12 g, 14 ml volume) – see Fig. 1. These were fitted with a cap and thermistor feed-throughs. Deuterium and hydrogen gases were produced by electrolysis of water/heavy water solutions at a range of various relative concentrations. Pre- and post-calibration runs were made with sand and Ar for each cylinder and thermistor assembly. All cylinders were pressurized to the same total 74 kPa (slightly above atmospheric at the lab’s altitude) by addition of Ar; the ratio of hydrogen, deuterium, and argon was varied so that the effect of changing deuterium partial pressures could be studied. The cylinders were simultaneously lowered into a constant temperature oil bath held at 80.0°C. The temperature differential between the internal temperature of the cylinder and the oil bath was recorded for each. The differential was recorded each minute and the average over 60 min. The standard deviation of the data points taken each minute was used to make error bar estimates.

The use of gas loading of powdered sample in LENR is well known [5]. The material used for this series was a fine powder – see Fig. 2.

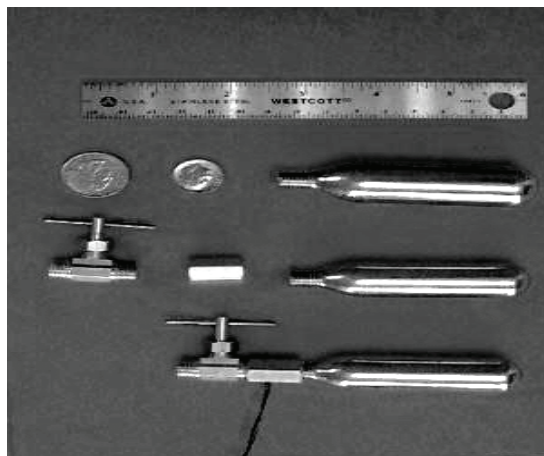


Figure 1. Palladium lattice. The big spheres are Pd atoms, their distance was set equal to 4; the octahedral sites lie on the same plane just in between two Pd atoms; the tetrahedral sites are positioned on a different plane at a relative distance of 2.828 Å.

4. Results

The results of the series of experiments can be seen in Table 1 and Lineweaver–Burk (LB) Plots in Fig. 3. This is a linear form of the Michaelis–Menten equation and produces a straight line with the equation $y = mx + c$ with a y-intercept

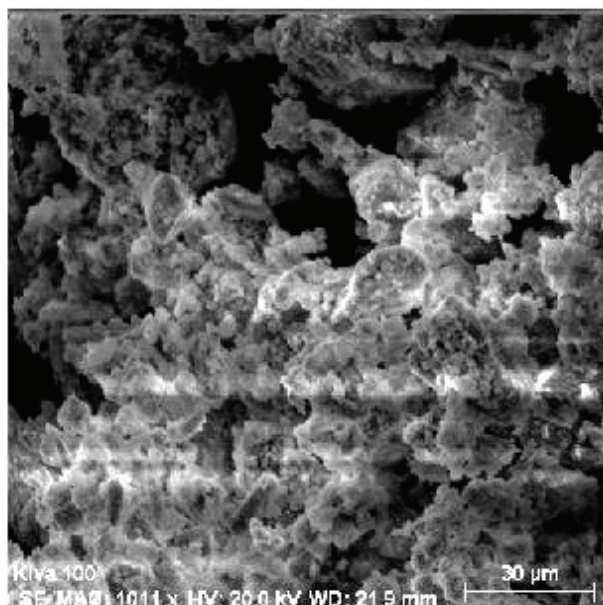


Figure 2. The electron micrograph shows the general size of the material used in the runs. All runs used the same material and 5 g sample size so the number and concentration of the active sites would remain approximately the same for easy comparisons. Photo courtesy of Edmund Storms.

equivalent to $1/V_{\max}$ or its modified form due to inhibitors and the extrapolated x -intercept of the graph representing $-1/K_m$. The extrapolated y -intercept is the case where an infinite concentration of deuterium would be available. Our units for the LB Plot are nonstandard since most enzyme and catalytic systems use molarities of chemical species in solution. Here we will use the reciprocal of the thermal output power for our y -axis as seen by our temperature differential between the sample inside its sheathed cylinder and the oil bath. Since our product of interest is heat, the differential is useful because it directly relates to the thermal power and hence the rate of “product” production. Likewise, instead of the standard molar concentrations used in most plots we will be using the partial pressures of the gases in units of kPa. Although the partial pressures were varied, the total pressure was always adjusted to 75 kPa, which was slightly above atmospheric pressure at lab elevation. The mathematical form is the same since the temperature differential versus partial pressure is the same form as rate of product production versus molar concentration.

From the LB plot in Fig. 3, it can be seen that there is an increase in the effective K_m due to the competition of hydrogen with deuterium for the active sites. The apparent increase in the effective K_m is indicative of competitive inhibition. This means that some active sites can be occupied either in part or totally by the hydrogen and there are fewer sites available for the deuterium pairs to proceed to the desired products. If this were the only role of the inhibitor, then the rate could recover by just increasing the concentration (pressure of gas) of the deuterium.

It can also be seen from the LB plot that the $V_{\max}$ is also lowered. This is indicative of non-competitive inhibition where the binding of the inhibitor is more tenacious than the reactants. Thus it appears that hydrogen not only competes with the deuterium in competitive inhibition but also, once bound, is not as easily separated from the active site as the deuterium. This leads to a lowering of the amount of heat generated per time (power) produced by our reaction. Hydrogen thus both competes for the active sites so that fewer deuterium–deuterium reactions can take place and ties up some active sites so that fewer sites are available for deuterium exchanges and thus lowers the ultimate temperature difference that can be reached by the reaction. When both competitive and non-competitive inhibition occurs, it is termed mixed inhibition. Mixed inhibition seems to be the case for these LENR gas-loading experiments. There is also a possibility that there is some product inhibition, which occurs when the accumulation of the product (for example He) inhibits the reaction. This must be investigated by using longer time runs than available in this experiment. It is likely that the role of the small particle size and elevated temperature may overcome some problems incurred by product inhibition. Dynamic changes in gas pressures may also limit such product inhibition. In our lock and key analogy, it is like having some locks break once opened. Until some of the nuclear ash is removed, some active sites are useless and the production rate starts to fall as time progresses.

Table 1. This shows the temperature differential seen at various partial pressures of deuterium and for various partial pressures of hydrogen. The remaining gas pressure was adjusted to a total of 75 kPa by addition of Argon. The estimated error bars for the temperature differentials is 0.04°C as seen from the time variation of the data readings over one hour. Error bars are not shown on the plot since reciprocals of the data points are plotted.

Deuterium Pressure kPa	Delta T with		
	0 kPa hydrogen	10 kPa hydrogen	20 kPa hydrogen
2	0.23	0.08	0.00
5	0.33	0.13	0.00
10	0.40	0.14	0.05
20	0.43	0.17	0.06
30	0.48	0.17	0.06
40	0.48	0.17	0.06
50	0.50	0.17	0.07
60	0.51	0.16	0.07

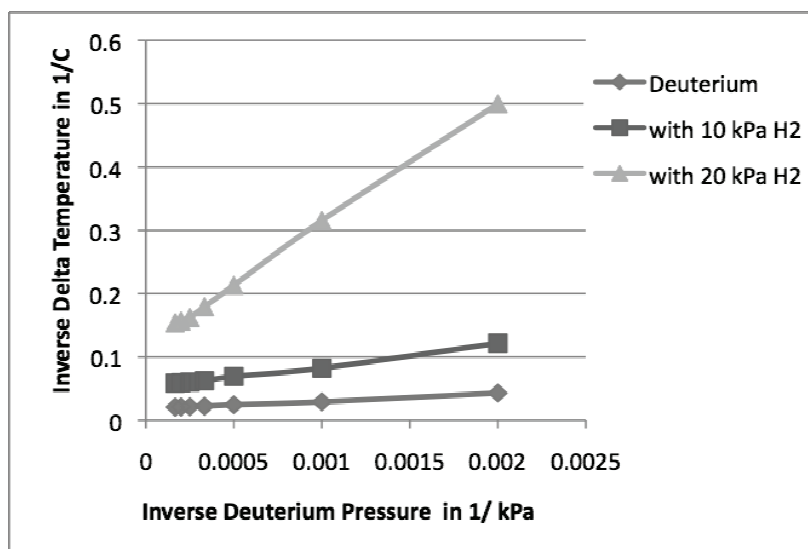


Figure 3. This is a plot of $1/\text{differential temperature } (^{\circ}\text{C})$ versus $1/\text{deuterium pressure (kPa)}$. As the hydrogen partial pressure increases the reaction rate decreases. The greater slope with increasing hydrogen pressure shows that the effective K_m increases, which lowers the reaction rates. The y-intercept also increases with increased hydrogen concentration, which signals a change in the effective V_{max} . This is indicative of hydrogen being bound more strongly than deuterium at the active site.

5. Discussion

The results show that hydrogen inhibits production of heat in LENR gas loaded systems by both competing for active sites and causing stable hydrogen/deuterium/active site complexes. This indicates that care should be taken to exclude the lighter hydrogen isotope from LENR gas loaded experiments. Practical advice would be to assure no cross contamination during preparation and the use of high vacuum and purging runs between any hydrogen and deuterium runs. Further preliminary experiments not included here would indicate that dynamic loading conditions, higher temperatures and higher surface area to mass metal hosts seem to give better results. That is to say the active sites for this series of experiments may reside on the surface interface between the deuterium gas and the catalytic host material and the reaction rate constants may be temperature dependent. This will be covered in a future extension of the kinetic model presented here.

Although this paper was designed to address LENR gas loaded systems, it is worthwhile to know that applications can be made to electrolytic systems. For example see run NRL684 in [6]. A close up of the relative part can be seen in Fig. 4.

In this experiment, Letts replaced D_2O with H_2O in an active co-deposited cell. There was an immediate disturbance due to the fluid replacement and then the cell first returns nearly to its original power levels. Then after about 30 min a steady drop was observed in “excess power” to about half the original value, then another slower decline to zero after about 9 h was observed. In light of this study, this seems to indicate that the first drop is due to the competitive portion of the inhibition from free exchange of H and D at the surface. This can be fairly fast since it involves the loading of the active sites from the solution. The second longer decline may be due to the non-competitive inhibition due to H slowly replacing, binding, and tying up active sites. One prediction of this model would be that the original power levels could be partially and temporarily recovered by increasing the current density during the competitive inhibition decline

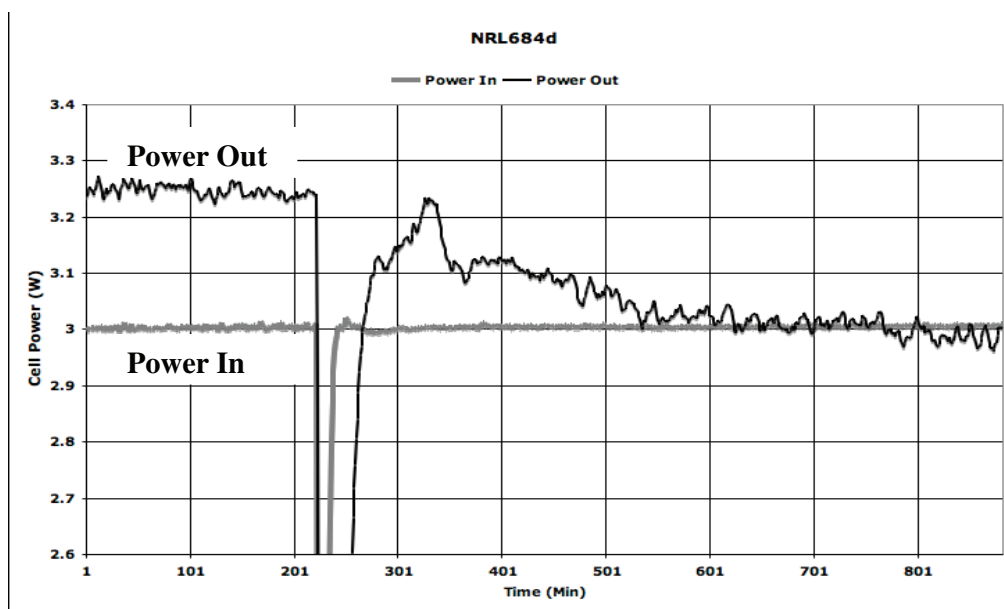


Figure 4. This is taken from Dennis Letts' work and is included elsewhere in this book. It is an electrochemical co-deposited run with the power in held at 3 W except during water addition. At point 210 the heavy water was replaced with natural abundance water. The system recovers for a while near point 310. There is then a first rapid decline over 30 min possibly due to competitive inhibition and finally a gradual decline to about point 800. This is perhaps due to slow replacement by H at the active sites as may be expected from non-competitive inhibition.

but not after the long non-competitive decline. Also it can be expected from this model that reversing the current and re-populating the active sites with hydrogen would destroy its heat production until completely cleaned of hydrogen.

It is refreshing to find that practical general guidelines and directions to the LENR process can be achieved from simple methods that avoid the assumptions of nuclear mechanisms and theories.

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