

The Thermodynamics and Kinetics of “HeaterMeals”

An Exercise in Undergraduate Inorganic Chemistry

William B. Jensen

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172; jensenwb@email.uc.edu

On a recent speaking trip to Ohio University, my host showed me a clipping from a local newspaper describing a new food product called “HeaterMeals”, which was being test-marketed in the Cincinnati area. According to the clipping, these packaged meals came complete with their own “stove” inside:

The stove has a patented food heater made of salt, iron, and magnesium. When salt water is added, it causes the iron and magnesium to produce heat and to thoroughly heat your meal!

Salt, iron, and magnesium were just too good a combination for an inorganic chemist to resist and, on returning to Cincinnati, I purchased several of these meals in order to explore the chemistry of their “inorganic ovens”. This chemistry turns out to involve a very clever use of elementary thermodynamics, kinetics, and inorganic electrochemistry.

Since this chemistry is easily understood by the average chemistry major, investigation of this product can serve as a stimulating undergraduate research project. For this reason, rather than simply summarizing what is in the patent literature, I have instead outlined my own course of investigation in order to illustrate what one can reasonably expect a good student to uncover by means of a few simple observations, test tube experiments, and access to a good technical library.

The Product

The product consists of a box containing a sealed food pouch that fits into a Styrofoam tray. Attached to the bottom of this tray is a large porous packet or “tea bag”, which contains the heater element (Fig. 1). There is also a plastic knife and fork, a napkin, and a packet of salt water. To operate the stove, the consumer pours the salt water into the tray and places the food pouch on top of the tea bag. One then slides the unit back into its box and 14 minutes later removes a fully heated meal.

The Role of the Magnesium

Use of a low-power binocular microscope to examine the heater element contained in the tea bag reveals that it consists of chunks of a silvery metal dispersed in a matrix of partly fused translucent spheres. Addition of the salt water to about half of a heater element placed in a shallow glass dish results in immediate reaction. There is violent effervescence, followed within seconds by rapid heating and the evolution of steam. The gas bubbles are flammable and can be ignited with a match, provided that this is done before too much steam accumulates. Examination of the heater element after the reaction ceases shows that the matrix of partly fused translucent spheres has remained intact but that the chunks of silvery

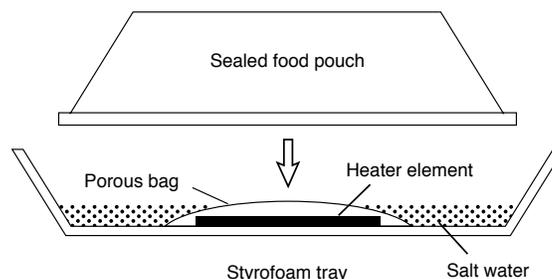
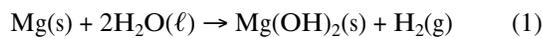


Figure 1. The components of a typical HeaterMeal.

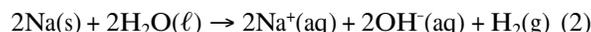
metal have either disappeared or have become coated with a white reaction product.

All of these observations are consistent with the hypothesis that the water oxidation of magnesium metal is the source of energy for the heater element:



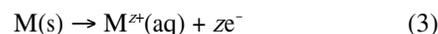
The observed white reaction product obviously corresponds to the magnesium dihydroxide and the flammable gas to the dihydrogen, whereas the translucent spheres correspond to some kind of inert material used to disperse the metal reactant and to retain most of the solid reaction products. Reaction 1 has an enthalpy value of -352.96 kJ/mol at STP—more than sufficient to account for the observed heat evolution (I).

Reaction 1 may be profitably compared with the reaction between sodium metal and water, which is often used as a chemical demonstration, and is normally considered to be an archetypal example of an energetically violent chemical reaction:



This reaction has an enthalpy value of -367.52 kJ/mol or nearly the same as reaction 1. Indeed, if one calculates enthalpies per mole of metal rather than per mole of reaction, then the water oxidation of magnesium metal is almost twice as exothermic as the corresponding reaction for sodium (-352.96 kJ/mol Mg versus -183.76 kJ/mol Na).

For students taking an inorganic course, this comparison between magnesium and sodium can be taken a step further using the cycle in Figure 2 to evaluate both their free energies of oxidation and their oxidation potentials. The free energy of oxidation (ΔG_{ox}), corresponding to the general equation



can be decomposed, in keeping with the cycle in Figure 2, into the sum of the free energies of atomization (ΔG_{a}), ionization (ΔG_{i}), and solvation (ΔG_{solv}):

$$\Delta G_{\text{ox}} = \Delta G_{\text{a}} + \Delta G_{\text{i}} + \Delta G_{\text{solv}} \quad (4)$$

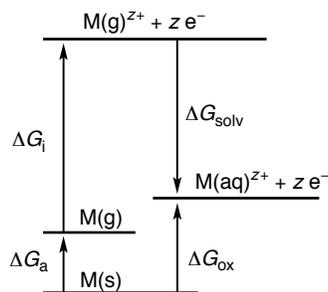


Figure 2. A thermodynamic cycle for the calculation of ΔG_{ox} for a given species M.

Table 1. Thermodynamic Data for the Evaluation of the Values of ΔG_{ox} and E_{ox} for Sodium and Magnesium

Species	ΔG_a / kJ	ΔG_f / kJ	ΔG_{solv} / kJ	ΔG_{ox} / kJ	E_{ox} / V
Mg	114.22	2191.16	-1903.30	402.8	2.36
Na	77.82	497.48	-410.03	165.27	2.73
H ₂	203.34	1313.36	-1088.68	428.02	0.00

The values for each of these terms, using the data of Sanderson, are given in Table 1, which shows an overall value of ΔG_{ox} for magnesium nearly two and a half times that of sodium (2). However, when these values are converted into oxidation potentials by conversion into volts, normalization relative to the moles of electrons involved, and subtraction from the value obtained for dihydrogen gas using the same cycle

$$E_{\text{ox}} = \Delta G_{\text{ox}}[\text{H}_2]/zF - \Delta G_{\text{ox}}[\text{M}]/zF \quad (5)$$

$$E_{\text{ox}} = 4.44 \text{ V} - \Delta G_{\text{ox}}[\text{M}]/zF \quad (6)$$

we again obtain a near equality in the final overall result, as shown in the last column of Table 1.

The Role of the Sodium Chloride

If students attempt to confirm the above conclusions, they will be rapidly disappointed. Despite the similarity in both their enthalpy values and oxidation potentials, sodium will give the expected violent reaction on contact with water, whereas magnesium will not. Only by strongly heating magnesium in steam is it possible to observe the reaction in eq 1 (3). In fact, a detailed study of the reaction between magnesium and water at room temperature, made by Roberts and Brown at the turn of the century, concluded that even after several weeks “magnesium is without action on distilled water, boiled to free it from gases and carefully cooled out of contact with air” (4).

Since thermodynamic calculations show that reaction 1 is extremely favorable at STP, failure to observe the reaction must be due to kinetic inhibition of some sort, and we do not need to look far for the probable cause. It has long been known that many metals which should react with water or spontaneously oxidize on contact with air do not do so because the hydroxides and oxides formed in the initial stages of the

reaction form a coherent film on the remaining metal and thus protect it from further attack. This phenomenon is referred to as “passivity” in the corrosion literature. As Ulick Evans observed in his 1926 volume on *The Corrosion of Metals* (5):

The only metals that react rapidly with pure water are those which have soluble hydroxides.

Inspection of the states in eqs 1 and 2 shows that they represent a classic example of the situation summarized by Evans. Magnesium dihydroxide is insoluble in water and blocks further reaction with the magnesium metal, whereas sodium hydroxide is soluble and does not inhibit continuous reaction between water and the metal surface.

Not only is insolubility a necessary condition for inducing passivity, the reaction product (P) must also have a unit volume (V/N) equal to or greater than that of the metal (M):

$$(V/N)_P / (V/N)_M \geq 1 \quad (7)$$

Otherwise an insufficient volume of product will be formed to replace the volume of metal that has reacted and thus produce a complete and coherent coating on the remaining metal. From dimensional analysis, it is apparent that the unit volume of a substance (V/N), usually measured in units of milliliters per mole and referred to as molar volume, is equal to its unit mass (m/N), measured in units of grams per mole, divided by its mass density (m/V), measured in units of grams per milliliter:

$$(V/N) = (m/N) / (m/V) \quad (8)$$

(where V = volume, N = particle population, m = mass) and thus that the ratio of the molar volume of the product to the molar volume of the metal is the ratio of their respective molecular weights multiplied by the inverse ratio of their respective densities:

$$(V/N)_P / (V/N)_M = \{(m/N)_P / (m/N)_M\} / \{(m/V)_M / (m/V)_P\} \quad (9)$$

The necessary data for magnesium metal and magnesium dihydroxide can be found in the *Handbook of Chemistry and Physics*. These show that a sufficient volume of magnesium dihydroxide is formed to provide more than complete coverage of the remaining magnesium metal:

$$(V/N)_{\text{Mg}(\text{OH})_2} / (V/N)_{\text{Mg}} = 1.77 \quad (10)$$

It should be noted that the condition in eq 7 is necessary but not sufficient for inducing passivity. The resulting solid product, though of sufficient volume, may conduct ions or electrons well enough to allow the reaction to continue, or it may be mechanically faulty owing to cracking or flaking and so fail to completely protect the underlying metal surface. In the case of magnesium, X-ray diffraction studies of the surface have confirmed that crystalline magnesium dihydroxide or “brucite” is formed during the immersion of pure magnesium in degassed distilled water and that the resulting film is “highly protective” (6).

However, it has also long been known that neutral solutions of the chloride ion cause magnesium metal to react with water at an observable rate at STP. Most of the paper by Roberts and Brown, quoted earlier, was devoted to a study of this phenomenon, and it has been the focus of much of the

corrosion literature on magnesium metal because it severely limits the use of magnesium and its alloys in the presence of sea water. As Evans noted in 1926 (5):

Magnesium, although scarcely affected by pure water, causes marked evolution of hydrogen when immersed in a solution of potassium chloride ... a film on an anode usually soon ceases to be protective if a small amount of a soluble chloride is added to the solution. ... What is quite certain is that the presence of chlorides in solutions tends to prevent the formation of a protective type of film on an anode.

Just how the chloride ion destroys the passivity of the magnesium dihydroxide film is still open to investigation. What is known is that the infinitely extended 6/3 layer structure of magnesium dihydroxide (Fig. 3) is highly susceptible to substitution of the hydroxide ions by chloride ions, leading to the formation of a variety of complex chlorohydroxides (Table 2), some of which (e.g., $Mg_3(OH)_5Cl \cdot xH_2O$) have actually been detected on the surface of magnesium metal that has been exposed to chloride solutions (6, 8, 9). Whether the structure changes accompanying chloride substitution in the brucite layer result in the layer failing mechanically or whether the resulting chlorohydroxides provide better ionic or electronic conductivity and hence lower overpotentials for dihydrogen discharge is still unknown. All that is certain is that the sodium chloride used in the HeaterMeals' "stove" functions kinetically to reduce the activation barrier for reaction 1, and that it does this by inhibiting the ability of the magnesium dihydroxide reaction product to form a passive coating on the magnesium metal.

The Role of the Iron

If students place a strip of magnesium metal, which has been freshly cleaned using sandpaper, in a neutral sodium chloride solution, they will observe the formation of dihydrogen gas bubbles on its surface, but at a rate far too slow to provide a practical heat source. The magnesium soon becomes coated with fine bubbles of dihydrogen gas, which block further reaction. This slow rate indicates the presence of a high activation energy or overpotential for hydrogen discharge at magnesium even in the absence of a coherent protective film of magnesium dihydroxide.

This problem can be eliminated by placing the magnesium in contact with a metal having a lower overpotential for hydrogen discharge, such as platinum, palladium, gold, copper, cobalt, nickel, or iron—of which iron is obviously the metal of choice from an economic point of view. The sites for the oxidation and reduction half-reactions are now spatially separated. Magnesium continues to oxidize to Mg^{2+} at the magnesium surface, whereas the water is now reduced to dihydrogen gas at the iron surface. This process is called galvanic corrosion or electrocatalysis. Figure 4, which is taken from the 1957 edition of Pauling's famous textbook, illustrates a simple classroom demonstration of the electrocatalysis of the Zn/H_3O^+ redox reaction using platinum or copper metal; Figure 5 graphically summarizes the electrocatalytic effects of various metals on the rate of magnesium corrosion in a 3% salt solution (10, 11). Note that iron is so effective that it drives the corrosion rate vertically off the graph.

Table 2. The Composition and Structure of Magnesium Dihydroxide and Various Magnesium Chlorohydroxides Obtained by Substitution of OH^- Ion by Cl^- Ion

Product	OH replaced (%)	Structure ^a
$Mg(OH)_2$ (Brucite)	0	$\frac{2}{3}[Mg(OH)_{6/3}]$
$Mg_3(OH)_5Cl \cdot xH_2O$	17	Unknown
$Mg_2(OH)_3Cl \cdot 4H_2O$	25	$\frac{1}{3}[Mg_2(OH)_3(H_2O)_3]Cl \cdot H_2O$
$Mg(OH)Cl$	50	$\frac{2}{3}[Mg(OH_{.5}, Cl_{.5})_{6/3}]$

^aFor background on these crystal coordination formulas, see ref 7.

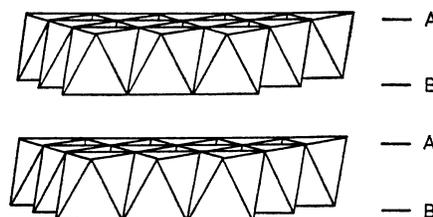


Figure 3. A coordinated-polyhedra model of the infinitely extended 6/3 layers found in $\frac{2}{3}[Mg(OH)_{6/3}]$. For background on the use of crystal coordination formulas, see ref 7.

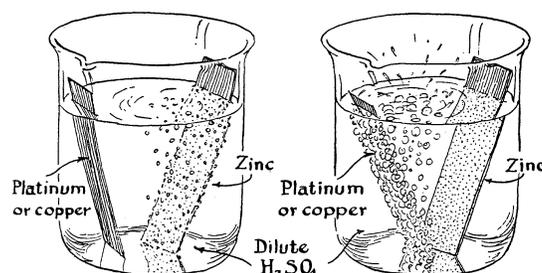


Figure 4. Electrocatalysis of the Zn/H_3O^+ redox reaction using platinum or copper metal. (Left) The zinc strip reacts with the H_3O^+ ion to produce dihydrogen gas, which rapidly coats the metal and inhibits further reaction. (Right) On touching the platinum strip to the zinc strip, reduction of H_3O^+ to dihydrogen is transferred to the platinum surface, which has a lower overpotential, while oxidation of the zinc continues unimpeded at the zinc surface (10).

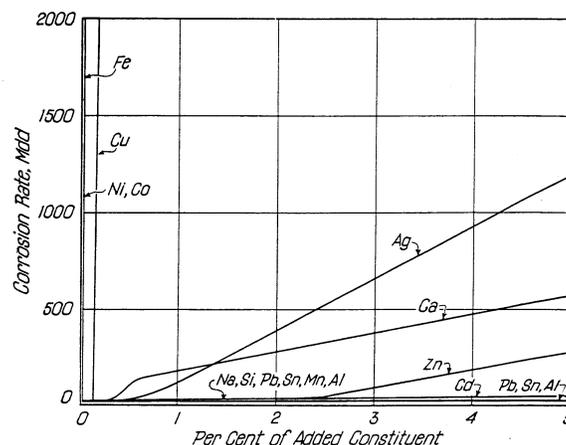
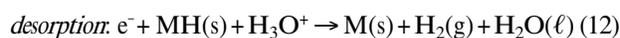
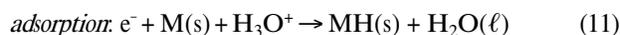


Figure 5. The electrocatalytic effect of various metals on the rate (measured as milligrams per decimeter per day) of magnesium corrosion in a 3% salt solution (11).

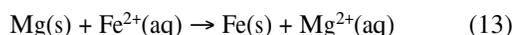
There is a vast literature dealing with the question of the electrochemical reduction of hydrogen at metal surfaces. Attempts have been made to correlate the ability of a given metal to lower the overpotential for dihydrogen discharge with the energy of hydrogen adsorption on its surface. A plot of the energy of hydrogen adsorption versus the rate of dihydrogen evolution (measured as the log of the exchange current i_0) is shown in Figure 6 for various metals. As can be seen, they fall into two groups, depending on whether the adsorption or desorption step for hydrogen reduction is rate limiting:



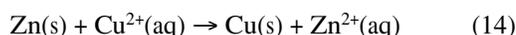
For most metals (Pt–Al), including iron, the desorption step (eq 12) is rate limiting, and the rate of discharge decreases with increasing adsorption energy. For Pb, Hg, Cd, and Tl, the adsorption step in eq 11 appears to be rate limiting, and the rate of discharge increases with increasing adsorption energy (12).

If one touches an iron wire to a strip of clean magnesium metal in a neutral salt solution, there is an immediate enhancement of the rate of dihydrogen evolution, though it is still nowhere near what is observed for the heater element. Increasing surface area by using magnesium turnings and iron filings, magnesium powder and iron powder, etc., leads to a further enhancement of the rate, but again does not come close to reproducing the violence of the heater element reaction. Obviously increasing the surface area of the solid reactants is the final key to increasing the rate of reaction 1 to the point where the rate of heat evolution results in a workable heater element.

As noted earlier, examination of the heater element under a low-power binocular microscope shows small chunks of only one kind of metal. Nothing that can be identified as separate pieces of iron is visible. This fact, coupled with the observation that the silvery metal has a slight gold- or bronze-like cast to it, suggested the possibility that the iron had been plated onto the magnesium by momentarily dipping the magnesium in a solution of an iron(II) salt, a reaction having a favorable net E° value of 1.93 V:



This idea was inspired by the classic work of Gladstone and Tribe, who in 1878 showed that the reducing properties of zinc were greatly enhanced by first dipping it in a copper sulfate solution to plate small microregions of copper onto its surface (13, 14). Here again the net E° value of 1.10 V is quite favorable:



Gladstone and Tribe explicitly recognized that the resulting “copper–zinc couple”, as they called it, was a micro-example of galvanically enhanced dihydrogen generation paralleling the macro-example shown in Figure 4, and their reduction couple still finds use as a reducing agent in organic chemistry (15). However, though the resulting iron-plated magnesium certainly displays enhanced dihydrogen evolution in salt water, the effect is again insufficient to account for the rates observed for the heating element.¹

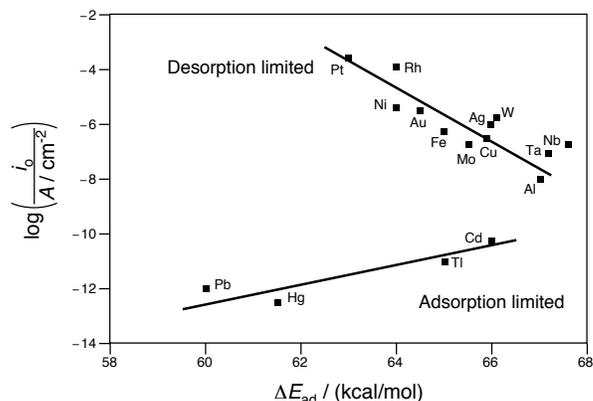


Figure 6. The correlation between energy of hydrogen adsorption and the rate of dihydrogen discharge (measured as $\log i_0$) for various metal electrodes (12).

The Patents

It was now time to check our results against the patent literature. The number listed on the “tea bag” containing the heater element was for a 1985 patent entitled *Flexible Electrochemical Heater* (16). This describes a method for making portable heating elements by pressureless sintering of mixtures of a “supercorrodng” powdered alloy of magnesium and iron with UHMW polyethylene powders in a mold for 20 min at 168 °C. The resulting heating elements can be made in any shape or size. The polyethylene matrix determines not only the shape and size of the heater element, it also serves to regulate both the density of alloy dispersal and the rate of salt water uptake, and acts as a containment system for the solid waste products. The sintered polyethylene obviously accounts for the partly fused translucent spheres that we observed under the microscope. As for the supercorrodng alloy, this was described as containing 5 atom % iron and as reacting with the salt water to generate heat and dihydrogen gas. It was also suggested that the thermal output of the heater element could be increased by dispersing chemicals, such as an $\text{MnO}_2/\text{Pd/C}$ mixture, in the matrix in order to catalyze the air oxidation of the dihydrogen gas generated by the alloy–salt water reaction.

Mention of a 5 atom % iron alloy of magnesium was initially puzzling, as examination of the phase diagram for the magnesium–iron system reveals that the two metals are virtually insoluble in one another (17, 18). A possible eutectic may exist between 0.0065 and 0.013 atom % iron, but even at 1200 °C iron is soluble only to the extent of 0.37 atom %. This puzzlement turned out to be based on an incorrect definition of an alloy. Most chemists I have polled seem, like me, to be under the false impression that an alloy must be a solid solution. As it turns out, it may in fact be a heterogeneous micromixture, which only appears homogeneous to the unaided eye. As defined by a well-known chemical dictionary (19):

Alloys are to be regarded as mixtures of metals rather than as compounds, although often metallic compounds are present in the mixture and may crystallize out; some alloys are solid solutions of one metal in another, others are mixtures of mutually insoluble metals.

The 1985 patent led, in turn, to a 1981 patent entitled *Supercorrodng Galvanic Cell Alloys for Generation of Heat and Gas (20)*. This revealed that the magnesium–iron alloy is indeed a micromixture made by blending the proper ratio of the metallic powders in a high-energy steel ball mill by “repeated flattening, fracturing and welding of the metal constituents.” According to the patent, during the milling process:

The energy of the impact of the colliding steel balls, with particles trapped between them, creates atomically clean particle surfaces. When these clean surfaces come in contact during collisions, they cold-weld together. An inert atmosphere in the mill prevents reoxidation on the clean surfaces. This also avoids oxide coatings on the particle surfaces which reduce cell reaction.

The resulting alloy particles are between 80 and 100 mesh in size and consist of isolated iron particles of the order of 30 μm embedded in a surrounding magnesium matrix—an elegant solution to the problem of maximizing the area of surface contact between the two metals.

Summary

In summary, the water oxidation of magnesium metal is the thermodynamic source of the heat for the HeaterMeal stove, with magnesium dihydroxide and dihydrogen gas as the immediate products. The sodium chloride or salt serves to kinetically enhance the rate of oxidation by preventing the formation of a coherent protective film of magnesium dihydroxide on the magnesium metal. The iron serves to kinetically enhance the rate of reaction by providing an alternative surface of low overpotential for the reduction and discharge of the dihydrogen gas.

Acknowledgments

My thanks to Peter Ramberg, Department of Chemistry, Johns Hopkins University, for bringing this product to my attention, and to Rudy Thomas, Department of Chemistry, University of Cincinnati, for his assistance in performing some of the experiments.

Note

1. Since, as a result of hydrolysis, aqueous solutions of iron(II) salts are acidic, we also compared the enhancement caused by dipping the magnesium in a dilute nitric acid solution of identical

pH. Though this caused an initial enhancement of dihydrogen evolution owing to the dissolution of the $\text{Mg}(\text{OH})_2$ film, it was notably less than that caused by dipping in the iron(II) solution.

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