Absorption and Desorption of Hydrogen in Metal Hydrides

by

Mohamed Said Shahat Ahmed El-Khatib

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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(Prof Dr. Vijay R. Raghavan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

November 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHAMED SAID SHAHAT AHMED EL-KHATIB

Abstract

The purpose of this project is to study the reaction rate during the absorption process of hydrogen in metal hydrides. Magnesium Hydride (MgH_2) was chosen to be the metal hydride material for the storage medium. A car was modelled to calculate the theoretical consumption of hydrogen fuel during an hour drive at a constant cruising speed. The reaction equilibrium constant was derived from Vant Hoff equation with variable values of operating conditions. Then, the rate equation role was to determine the reaction rate of the absorption process of hydrogen by magnesium. This report contains new aspects, which show the conditions of obtaining hydrogenation rates and represents new approach of improvement of hydrogen absorption process in light metals, such as magnesium, that can provide promising results for the hydrogen storage applications.

ACKNOWLEDGMENT

In the name of God; the most merciful and the compassionate, I Mohamed Said Shahat Ahmed El-Khatib would like to take this opportunity to thank all the people who have given help, support and encouragement to me during my Final Year Project.

I would like to express my deep appreciation to my supervisor, Prof Dr. Vijay R. Raghavan for his support, attention, guidance and patience through the project execution, and his willingness to discuss my project at any time. I could not have asked for a better supervisor than Prof Dr. Vijay. His attention to details of my research, and his advice has made my FYP an extremely rewarding experience. His passion for mechanical engineering has really inspired me. Special appreciation and gratitude to my loving parents even though I was half a world away. Thank you for your patience and prayers, I love you both more than anything in the world. I owe special thanks to the other lecturers of Mechanical Engineering Department for all their suggestions, comments and discussions for improvement of this work during seminars and presentations.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Hydrogen is the simplest element known to man. Each atom of hydrogen has only one proton. It is also the most plentiful gas in the universe. Stars are made mainly of hydrogen. Hydrogen has the highest energy content of any common fuel by weight (about three times more than gasoline), but the lowest energy content by volume (about four times less than gasoline). It is the lightest element, and it is a gas at normal temperature and pressure. Hydrogen has great potential as an environmentally clean energy fuel and as a way to reduce reliance on imported energy sources.

At normal temperature and pressure, hydrogen is a colorless and odorless gas with no toxic effects. It is the lowest density element with a density of 0.09 kg/m3 at ambient conditions. After helium, hydrogen has the lowest melting and boiling points (-259 °C and -253 °C). Hydrogen is highly inflammable with broadly spaced ignition limits in air (lower explosion limit 4 % by volume, upper explosion limit 76 % by volume) and low ignition energy (0.017 mJ for a stoichiometric air mixture). If burnt hydrogen has a high adiabatic flame temperature of 2100 °C and a high laminar burning velocity of up to 2.7 m/s. As with all fuels, the use of hydrogen requires compliance with safety regulations, like keeping away ignition sources and taking precautions against electrostatic charge. Because hydrogen is a very light and diffusive gas, increasing concentrations can normally be prevented easily through adequate ventilation.

As an energy carrier and with respect to fossil fuels, hydrogen has advantages with regard to environmental impact and availability. Hydrogen is the only available carbon free fuel and thus can be burnt without the emission of carbon dioxide CO_2, particles C, and hydrocarbons HC. Combustion of hydrogen H_2 with oxygen O_2 takes place and yields water H_2O. If burnt in a fuel cell in a so called cold combustion, it yields electric energy free of emissions. If burnt in a hot combustion in an internal combustion engine, hydrogen has the highest gravimetric calorific value of all fuels (H_u = 120 kJ/kg = 33,3 kWh/kg). Due to the high temperatures in internal combustion engines the combustion with air emits nitron oxides NO_x, which can be reduced by applying high air excess ratios.

Hydride is the name given to the negative ion of hydrogen, H^-. Although this ion does not exist except in extraordinary conditions, the term hydride is widely applied to describe compounds of hydrogen with other elements, particularly those of groups 1–16. The variety of compounds formed by hydrogen is vast, arguably greater than that of any other element. Various metal hydrides are currently being studied for reversible on-board hydrogen storage and release at low temperatures and pressures, such as in fuel cell-powered electric cars and in batteries. The group 14 hydrides are already of vast importance in storage battery technologies. They also have important uses in organic chemistry as powerful reducing agents, and many promising uses in hydrogen economy.

Metal hydrides are powders whose particles are typically a few microns in size. When these metal powders absorb hydrogen to form hydrides, heat is released (exothermic reaction). Conversely, when heat is absorbed (endothermic reaction), hydrogen is released from the hydride. In the absorption process, hydrogen gas molecules break down into hydrogen atoms and penetrate into the interior of the metal crystal to form a metal hydride. In the desorption process, hydrogen atoms migrate to the surface of the metal hydride, combine into hydrogen molecules and flow away as hydrogen gas, allowing the material to form the original metal structure.

1.2 Problem Statement

1.2.1 Problem Identification

Hydrogen is the most abundant element in nature and thus theoretically in unlimited supply. However, as a result of its high reactivity, hydrogen is practically only encountered in compounds and thus has to be isolated through the use of primary energy. Hydrogen can be generated through a number of methods from a variety of sources, best and free of CO_2 through electrolysis from water in the reverse reaction. If electricity is taken from alternative sources like water, wind, or solar power, the production and combustion of hydrogen in a renewable energy loop becomes possible. This production is expensive and at the moment not competitive to fossil fuels. Also due to its low density, storage of hydrogen still poses a challenge.

Since the energy shortage and environment requirement are getting more and more serious, developing a new kind of clean energy attracts many scientists and engineers who come from different fields. The study of hydrogen absorption/desorption by metals and alloys has been paid a special attention due to its efficiency, convenience and extensive sources. A large amount of experiments concerning hydrogen storage in alloy have been done and more new experiments will be continued [1,2].

However, the theoretical treatment for thermodynamics of hydrogen storage is still not satisfactory in comparison with the experimental study [3]. It is because, the absorption/desorption of hydrogen is very complicated.

1.2.2 Significance and Relevancy of the Project

The mechanism of this process consists of a series of sequential steps [1,3-7]. If one treats each step rigorously, that will lead to solve a group of differential equations or integral equations. The situation now is that some treatments are so complicated that cannot offer an explicit analytic expression and cannot give an intuitionist quantitative discussion. From the point of view of practical application it is desired to have a simpler and physical meaningful explicit analytic expression, which is convenient for use and can still give a good prediction under an acceptable simplified assumption.

In order to maintain a low weight and volume of hydride, it is critical to maintain short cycle times for charging and discharging hydrogen. Heat transfer is the rate limiting process that controls hydrogen uptake or removal and is determined by the effective thermal conductivity of the hydride. The dynamic response of a hydrogen storage system is important in the design of metal hydride based energy conversion. Hence it is necessary to predict transient heat and mass transfer in the metal hydrides.

The problem then is to devise suitable methods to calculate the variation in the hydride particle reactivity as a function of the hydrogen concentration. As well as, to find the reaction rate of the charging process this determines the time of the reaction.

1.3 Objectives and Scope of Study

This project is stressed on obtaining simple thermodynamic formulas to express the relation between the absorption/desorption of hydrogen and other related physical properties under a reasonable simplified assumption and that might not sacrifice too much calculation accuracy.

The time frame of this project is twelve months. The first six months; which is considered as the Final Year Project 1st semester; concentrates on hydrogen storage absorption and desorption rates. The other six months; which is considered as the Final Year Project 2nd semester; will concentrate on further researches to supply more methods for calculating the thermodynamics of absorption and desorption of hydrogen, and to study more about the improvement of hydrogen storage systems.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Vant Hoff Equations

The van't Hoff equation (also known as the van't Hoff isochore) in chemical thermodynamics relates the change in temperature (T) to the change in the equilibrium constant (K) given the standard enthalpy change (ΔH^o) for the process [8]. The equation was first derived by Jacobus Henricus van't Hoff.

$$\frac{\mathrm{dlnK}}{\mathrm{dT}} = \frac{\Delta \mathrm{H}}{\mathrm{RT}^2}$$

Equation **1**

If the enthalpy change of reaction is assumed to be constant with temperature, the definite integral of this differential equation between temperatures T_1 and T_2 is given by

$$\mathrm{Ln}\left(\frac{K_2}{K_1}\right) = \frac{-\Delta \mathrm{H}}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Equation **2**

In this equation K_1 is the equilibrium constant at absolute temperature T_1 and K_2 is the equilibrium constant at absolute temperature T_2. ΔH^o is the standard enthalpy change and R is the gas constant.

Since

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta S$$

Equation **3**

and

$$\Delta G = -RT\ln K$$

Equation **4**

It follows that

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Equation **5**

Therefore, a plot of the natural logarithm of the equilibrium constant versus the reciprocal temperature gives a straight line. The slope of the line is equal to minus the standard enthalpy change divided by the gas constant, $-\Delta H^o/R$ and the intercept is equal to the standard entropy change divided by the gas constant, $\Delta S^o/R$. Differentiation of this expression yields the van 't Hoff equation.

2.2 Rate Equation

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with concentrations or pressures of reactants and constant parameters (normally rate coefficients and partial reaction orders) [9]. To determine the rate equation for a particular system one combines the reaction rate with a mass balance for the system [10]. For a generic reaction $mA + nB \rightarrow C$ with no intermediate steps in its reaction mechanism, the rate is given by

$$r = k[A]^m[B]^n$$

Equation **6** General Rate Equation

Where [A] and [B] express the concentration of the species A and B, respectively (usually in moles per liter (molarity)); m and n are the respective stoichiometric coefficients of the balanced equation, otherwise they must be determined experimentally; and k is the rate coefficient or rate constant of the reaction. The value of this coefficient k depends on conditions such as temperature, ionic strength, and surface area of the adsorbent or light irradiation. For elementary reactions, the rate equation can be derived from first principles using collision theory. Again, m and n are not always derived from the balanced equation.

The rate equation of a reaction with a multi-step mechanism cannot, in general, be deduced from the stoichiometric coefficients of the overall reaction; it must be determined experimentally. The equation may involve fractional exponential coefficients, or it may depend on the concentration of an intermediate species.

2.2.1 First-Order Reaction

A first-order reaction depends on the concentration of only one reactant (a uni-molecular reaction). Other reactants can be present, but each will be zero-order. The rate law for an elementary reaction that is first order with respect to a reactant A is

$$\mathrm{r} = -\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k[A]}$$

Equation **7** First-Order Reaction Rate Equation

Where k is the first order rate constant, which has units of 1/time.

The integrated first-order rate law is

$$\ln[\mathrm{A}] = -\mathrm{kt} + \ln[\mathrm{A}]_0$$

Equation **8** Integrated First-Order Law

A plot of $\ln[\mathrm{A}]$ vs. time t gives a straight line with a slope of $-\mathrm{k}$.

2.2.2 Second-Order Reaction

A second-order reaction depends on the concentrations of one second-order reactant, or two first-order reactants. For a second order reaction, its reaction rate is given by:

$$r = k[A]^2 \qquad \text{or} \qquad r = k[A][B] \qquad \text{or} \qquad r = [B]^2$$

Equation **9** Second-Order Rate Equation

Another way to present the above rate laws is to take the log of both sides:

$$Ln[r] = \ln k + 2\ln[A]$$

Equation **10** Second-Order Rate Equation

2.3 Hydrogen Storage Characteristics of Commercial Mg and MgH_2

2.3.1 Absorption

Hydrogentation/dehydrogenation studies of commercial Mg date almost 50 years back to the pioneering studies of Stampfer et al. [11] and Kennelley et al. [12,13]. The former authors reported the enthalpy of MgH_2 formation being in range of -70.8 to -72.6 kJ/mol and corresponding entropy as -127.3 to -130.6J/molK.

The latter authors reported the heat (enthalpy) of formation of MgH_2 as -74.1 ± 2.9 kJ/mol. Vigeholm et al. [13-17] carried out very through investigations of hydrogen absorption/desorption of commercially pure Mg. It was concluded that any comminuted Mg product with characteristics dimensions of less than approximately 75 µm and with impurity concentrations and compositions typical of normal Mg products will absorb hydrogen readily above 300°C at pressures exceeding the equilibrium level.

It was claimed that activation was in general either unnecessary or required only a few cycles under normal absorption conditions. The highest absorption rate was observed at an optimal temperature of around 340 - 350°C. Increasing the temperature above this value had slightly adverse effect on absorption kinetics. At about 236°C and 1.2 MPa hydrogen pressure, the magnesium powder absorbed about 2.3 wt.% H_2 in roughly 6,000 seconds. At about 340°C, the same powder absorbed about 5.4 wt.% H_2 in roughly 3,600 seconds. At the range of absorption temperature up to 340°C, the increase of pressure above 2 MPa increased the initial rate of kinetics but simultaneously reduced the degree of conversion of Mg into Mg H_2.

In general, in order to obtain the degree of reaction close to 100% (i.e., Mg completely converted to a nearly single phase Mg H_2), the absorption temperature had to be higher than 400°C at a moderate hydrogen pressure of about 2.0 – 2.5 MPa. In absorption process, the reaction of magnesium with hydrogen is a nucleation and growth mechanism where the nucleation rate is pressure dependent. It was estimated that the enthalpy and corresponding entropy of Mg H_2 formation as -70.0 kJ/mol and -126 J/molK, respectively.

2.4 Thermodynamic optimization of the system magnesium–hydrogen

Because of its high hydrogen content of 7.6 wt% and due to enthalpy changes resulting from formation and decomposition respectively, magnesium hydride MgH_2 is interesting both as hydrogen absorbent and heat absorbent at medium temperatures.

Accordingly, there is a large number of published results covering the formation and decomposition equilibrium presented by the known pressure/composition isotherms [18-27]. The thermodynamic evaluation of these experimental results is usually based upon the van't Hoff equation. Thus, values for the enthalpy of formation $\Delta_f H$ and for the entropy of formation $\Delta_f S$ are resulting.

A comparison between the $\Delta_f H$ and $\Delta_f S$ values by different authors [31,32] indicates considerable deviations (about 7%), which are still magnified, if equilibrium pressures are concerned. These considerable differences are caused by the following, frequently unconsidered factors: very slow adjustment of equilibrium, temperature dependence of $\Delta_f H$ and $\Delta_f S$, hysteresis between pressure of formation and pressure of decomposition, the real behavior of gaseous hydrogen and the solubility of hydrogen in magnesium (α-MgH_x, $0 < x < 0.1$).

On the basis of different experimental data an optimized record for the thermodynamic description of both the phase and the reaction equilibrium can be obtained. The experimental data [19, 21, 25 ,26] are derived from equilibrium measurements and from calorimetric measurements of our own [28,29].

Experimental investigations on the thermodynamic properties of the system Mg–H nearly exclusively are based upon the measurement of equilibrium pressures as a function of temperature. In Table 1 values of enthalpy of formation and entropy of formation, derived from those measurements, are given. The considerable scattering of the values does not allow the derivation of optimized values on that basis. Only in a few cases the original measured values ($p = f(T)$) are reported [19,21,25,26].

Table **2.1** Enthalpies and entropies of formation for MgH_2

$\Delta_f H$ (kJ mol^{-1})	$\Delta_f S$ (J K^{-1} mol^{-1})	Temperature Ranges (°C)	References
-70.1	-126.0	303-390	[19]
-73.1	-135.8	440-560	[20]
-74.0		380-480	[18]
-74.1		234-278	[21]
-74.3	-136.0	280-370	[24]
-74.7	-135.3	320-480	[27]
-77.4	-138.3	300-350	[22]
-80.9	-144.8	300-450	[25]
-81.2	-146.1	270-345	[26]
-85.0	-137.0	280-360	[23]

On the basis of heat capacity measurements by means of adiabatic low temperature calorimetry within the temperature range from 15 to 300 K [28] and within the temperature range from 290 to 360 K, we determined the molar standard entropy and the temperature behavior of heat capacity $C_p(T)$ within the range 15–360 K for magnesium hydride.

CHAPTER 3

METHODOLOGY

This chapter covers the analysis techniques, the project execution flow and Gantt charts for FYP II.

3.1 Analysis Technique

Project consists information gathering on absorption rates of hydrogen in metal hydrides as a literature review. After getting familiar with hydrogen storage systems, the methods of calculating the absorption process of hydrogen are modeled with the guide of scientific thermodynamic equations. Magnesium metal was chosen to be the storage material for hydrogen storage. A simple car model is done to determine the consumption of hydrogen needed for assumed travelling details. Then, the time needed to absorb the calculated mass of hydrogen is calculated by linking together the scientific equations reviewed before. The mathematical model of the reaction is converted to simple formulae which are used in Microsoft Excel software to determine the effect of temperature on the absorption reaction.

3.2 Procedure Identification

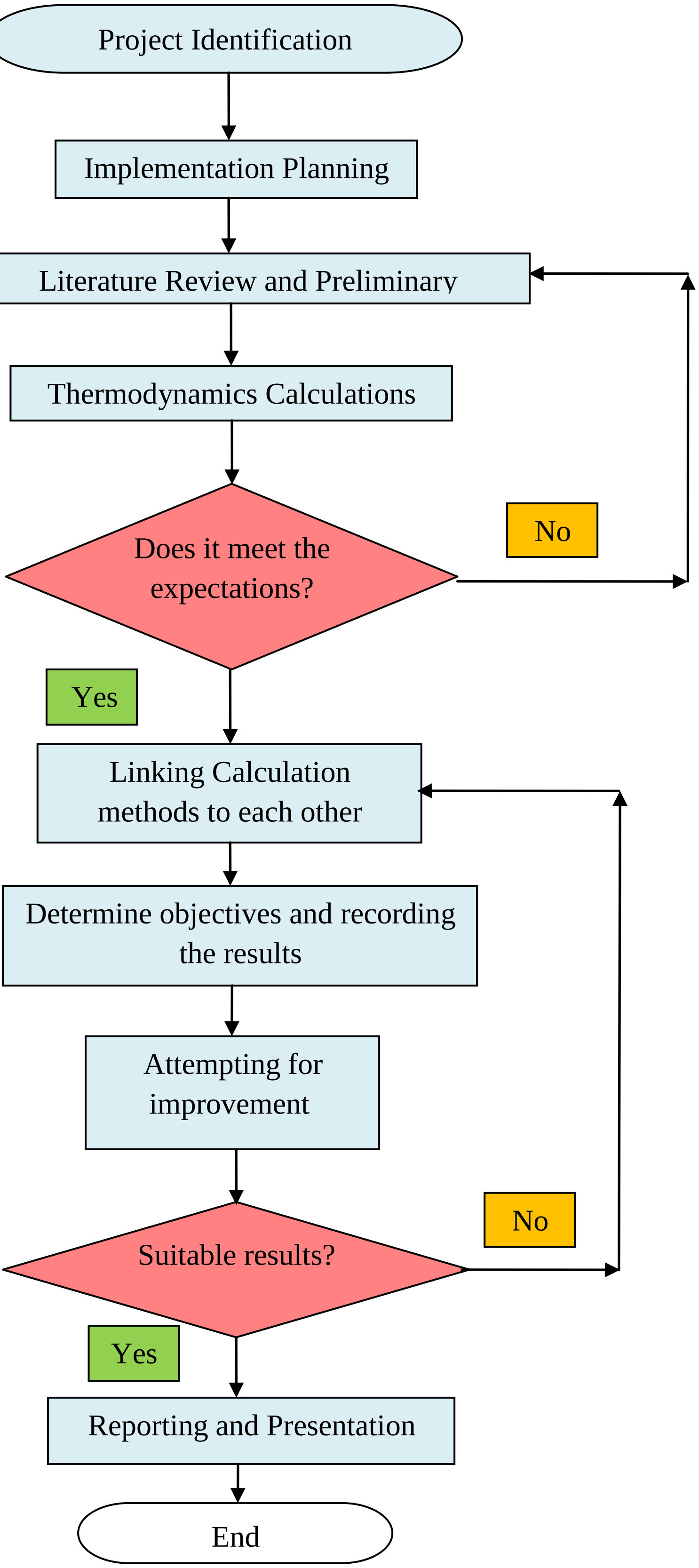


Figure **3.1** Procedure Flow Chart

3.3 Gantt Chart

The purpose of the project is to develop a framework, which will enhance knowledge skills in the process of applying it, expanding thoughts, solving problems independently and presenting findings through minimum guidance and supervision. The first priority to complete this project successfully is time consuming. In Table 3.1 a Gantt chart is done to organize the project time schedule during the semester. Furthermore, the Gantt chart includes Key Milestones to determine the submission dates for reports and seminars.

Table **3.1** Gantt Chart for FYP II

No.	**Detail/ Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		**10**	**11**	**12**	**13**	**14**	**15**
1	Project Work Continues	🟫	🟫	🟫							**Mid-semester break**						
2	Submission of Progress Report I				●												
3	Further Research on Case Study				🟫	🟫	🟫	🟫	🟫	🟫							
4	Submission of Progress Report II								●								
5	Seminar (compulsory)								●								
6	Project Work Continues											🟫	🟫	🟫	🟫		
7	Poster Exhibition													●			
8	Submission of Dissertation (Soft Bound)															●	
9	Oral Presentation																●
10	Submission of Dissertation (Hard Bound)											After Oral Presentation by 7 days					

● Suggested Milestones

🟫 Process

The process flow of FYP II starts with further researches in the first three weeks, and the Progress Report I is submitted at the 4th week. Further researches on the project's case study and literature review start from the 4th week until the 9th week. The submission of Progress Report II and its seminar are at the 8th week. After the mid-semester break, the project research and progress continues until the 13th week. The poster exhibition for the pre-EDX is at the 10th week, while the poster exhibition is held on the 12th week. Hopefully, the submission of the soft copy dissertation will be at the 14th week. The oral presentation is on 15th week where the study week for this semester is withheld. Finally, the hard copy dissertation will be submitted one week after the final presentation.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material Selection

The hydrogen storage capacity per unit weight of typical metal alloys is very low (about 2.2 mass%) and not sufficient for use in a fuel cell vehicle. Therefore, alloys containing light elements are focused on high performance storage materials. Most hydrogen absorbing metals are very reactive, easily forming surface oxides which then block the uptake of hydrogen. They also require costly time consuming activation. Magnesium, in particular has a high storage capacity (7.6 wt.%) with the benefit of the low cost of the abundantly available magnesium [33-35].

For this reason, magnesium and its alloys are considered to be some of the most important candidates for reversible hydrogen storage materials. Unfortunately, magnesium hydrides have some impediments. The main barriers for direct usage of pure MgH_2 are slow desorption kinetics, a high thermodynamic stability and a high reactivity toward air and oxygen which it has in common with most other lightweight metal hydrides [35-37]. The high thermodynamic stability of MgH_2 results in a relatively high desorption enthalpy, which corresponds to an unfavourable desorption temperature (> $300^{o}C$) at 1 bar H_2.

To enhance the metal hydride selection, it was chosen to obtain magnesium hydride (MgH_2) and then to activate this compound by reactive ball milling of Mg powder, followed of chemical activation by surface modification of Mg powder with nickel ultrafine particles addition. Thus magnesium can become an efficient material for hydrogen storage.

Magnesium metal transforms into magnesium hydride in a gas-solid reaction, according the following chemical reactions:

$$Mg + H_2 \leftrightarrow MgH_2$$

In the solid phase MgH_2 forms a hydride bridged polymer, such as presented in Figure 1, that confer a high stability.

Figure **4.1** Schematic representation of solid phase MgH_2

The hydriding reaction of metallic magnesium involves several steps:

(1) Gas permeation through the particle bed,
(2) surface adsorption and hydrogen dissociation,
(3) migration of hydrogen atoms from the surface into the bulk,
(4) diffusion through the particle and finally
(5) nucleation and growth of the hydride phase.

In principle each of these steps might be rate limiting.

4.2 Car Model

Theoretical amount of hydrogen could be calculated by using the following assumed factors according to several references:

- Constant speed of 80 km/h to travel 80 km (1 hour drive)
- Mass of car is 1200 kg
- Drag coefficient of 0.25 (C_d) [38]
- Rubber has a Poisson ratio of nearly 0.30 [39]
- At sea level and 25 °C, air has a density of approximately 1.3 kg/m^3 [40]
- Frontal projected area is 2.04 m^2
- Engine efficiency is taken to be 0.40 (η_{engine}) [41]

4.2.1 Frontal Projected Area

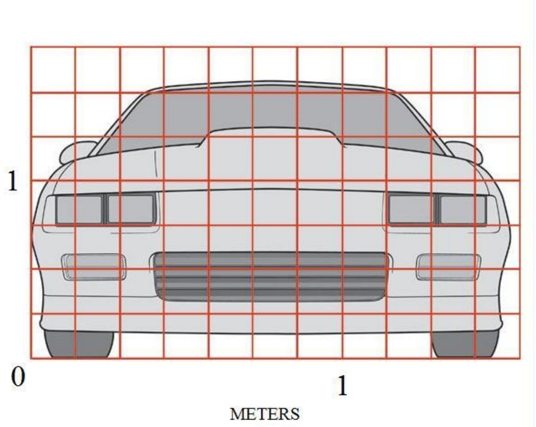


Figure **4.2** Car Frontal Projection

The frontal projected area of the car could be calculated according to the dimensions assumed.

$$\text{Area} = (0.8\times1.5) + (0.7\times1.2) = 2.04\ \text{m}^2$$

To calculate the total power needed [38] for the car to cruise through on 80 km/h, we have to calculate the power to resist the air drag and the power of friction of the tires with the discrete surface.

$$P_t = P_f + P_d$$

Equation **11** Total Power

4.2.2 Frictional Power

The normal force is the force pushing up on the tires. Caused by the weight of the vehicle and tires, it is in fact equal in size (but opposite in direction) to the weight pressing down on the ground.

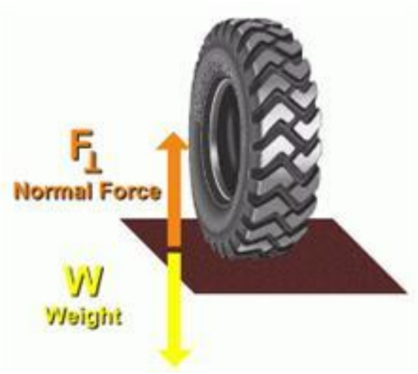


Figure **4.3** Normal Force

However, since the weight of the tires is only a small percent of the total weight of the vehicle, tires that weigh more only cause a small increase in traction.

The coefficient of friction is a number that is determined by the nature of the two surfaces in contact. The 'rougher' the two surfaces are relative to each other, the bigger this number will be. Thus, the larger the friction forces.

Figure **4.4** Coefficient of Friction

When a tire meets dry pavement on a highway, the two surfaces that are in contact are rubber and asphalt. The amount of area in contact between two discrete surfaces does not affect the force of friction; whether the tire has treads or not is irrelevant.

The friction equation calculates the frictional force [38] applied on an object from a frictional surface at a relative velocity.

Friction force = Normal force × Poisson ratio

= (1200 × 9.81) × 0.30

= 3531.6 N

Velocity = 80 km/h = 80 × (1000/3600) = 22 2/9 m/s

The power needed to overcome the frictional force is given by

P_f = Friction force × Velocity

$P_f = (3531.6) \times (22\ 2/9) = 78480$ W = 78.48 kW

The drag equation [38] calculates the drag force experienced by the car moving through a fluid at the relative velocity. The drag force includes the aerodynamic resistance, rolling resistance, engine friction and other losses.

$F_d = 0.5\ \rho v^2 A C_d$

$= (0.5) \times (1.3) \times (22\ 2/9)^2 \times (2.04) \times (0.25)$

= 163.7 N

The power needed [38] to push an object through a fluid increases as the cube of the velocity is the external power. The power required to overcome the aerodynamic drag is given by

P_d = Drag force × Velocity

= (163.7) × (22 2/9)

= 3638 W = 3.638 kW

Then,

$P_t = 78.48 + 3.638 = 82.118$ kW ≈ (110 hp)

Theoretical Power = Total power / Engine efficiency

= 82.118 / 0.40 = 205.295 kW

Since the modeled car is to travel 80 km with a speed of 80 km/h, then it is a one hour drive.

Then the one hour theoretical energy = 205.295 × 3600 = 739062 kJ
Then the theoretical quantity of hydrogen [42] = 5.26 kg

4.3 Rate of Reaction

According to the references mentioned above [18-32] for the enthalpy and entropy values, and by using the Vant Hoff equation [Equation **5**], the values of equilibrium constant (k) could be determined depending on variable values of temperature.

Table **4.1** Equilibrium Constant values

Temperature (K)	**$\Delta_f H$ (kJ mol^{-1})**	**$\Delta_f S$ (J K^{-1} mol^{-1})**	**ln k**	**k (s^{-1})**
507	-74.1		-15.15446569	2.62119E-07
543	-81.2	-146.1	-15.15445468	2.62122E-07
553	-74.3	-136	-15.15445188	2.62123E-07
573	-77.4	-138.3	-15.15444657	2.62124E-07
576	-70.1	-126	-15.1544458	2.62125E-07
593	-74.7	-135.3	-15.15444161	2.62126E-07
653	-74		-15.15442856	2.62129E-07
713	-73.1	-135.8	-15.15441771	2.62132E-07

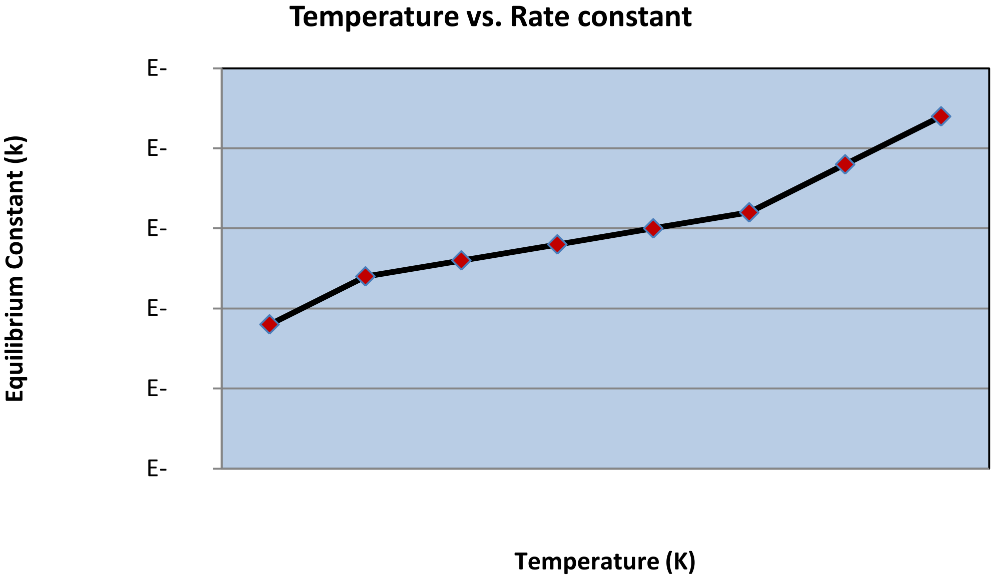


Figure **4.5** Temperature effect on Equilibrium Constant

As it can be seen from the above graph, that equilibrium constant is directly proportional to the temperature applied to the reaction. As a result, very high temperatures seem to do not affect the equilibrium constant much.

Since the mass hydrogen needed to react in the charging process is 5.26 kg, and by having the molecular weight of hydrogen (MW) [43] of 2.016 kg kg^{-1} mol^{-1}. Then the number of moles in the reaction is

$$n = \frac{m}{MW} = \frac{5.26}{2.016} = 2.609126984 \text{ moles}$$

Equation **12** Number of Moles equations

Moreover, since the density of hydrogen (ρ_H) [44] is 0.0899kg m^{-3}. Then the volume of hydrogen could be estimated as

$$V = \frac{m}{\rho} = \frac{5.26}{0.0899} = 58.50945495 \text{ m}^3$$

Equation **13** Volume of Hydrogen

Hence, the concentration of hydrogen in the hydrogenation process according to its mass could be derived as

$$[A] = C = \frac{n}{V} = \frac{2.609126984}{58.50945495} = 0.044593253 \text{ mol m}^{-3}$$

Equation **14** Concetration of Hydrogen

Next step is to determine the reaction rate (r) according to the first-order reaction equation [Equation **7**], and depending on the variable values of k affected by ranges of temperature in Table 4.1.

Table **4.2** Reaction Rate values

k (s^{-1})	**[A] (mol m^{-3})**	**r (mol m^{-3} s^{-1})**
2.62119E-07	0.044593253	1.16888E-08
2.62122E-07	0.044593253	1.16889E-08
2.62123E-07	0.044593253	1.16889E-08
2.62124E-07	0.044593253	1.1689E-08
2.62125E-07	0.044593253	1.1689E-08
2.62126E-07	0.044593253	1.1689E-08
2.62129E-07	0.044593253	1.16892E-08
2.62132E-07	0.044593253	1.16893E-08

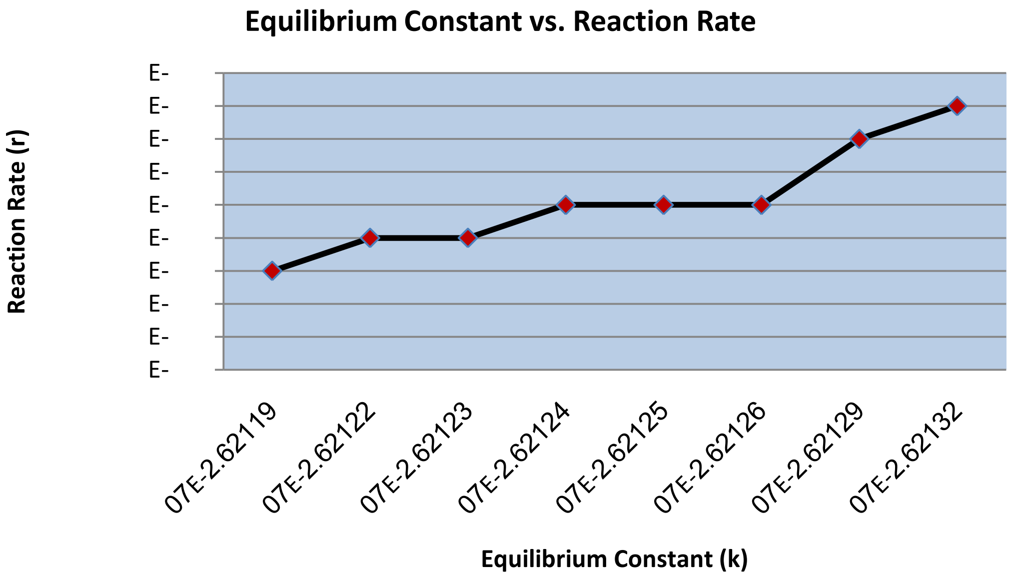


Figure **4.6** Equilibrium Constant effects on the Reaction Rate

4.4 The effect of Surface Area on Reaction Rates

It is described and explained that the effect of changing the surface area of a solid on the rate of a reaction it is involved in. This applies to reactions involving a solid and gas. Solid also could be acting as a catalyst.

The more finely divided the solid is, the faster the reaction happens. A powdered solid will normally produce a faster reaction than if the same mass is present as a single lump. The powdered solid has a greater surface area than the single lump.

Imagine a case of a very fine powder reacting with a gas. If the powder was in one big heap, the gas may not be able to penetrate it. That means that its effective surface area is much the same as (or even less than) it would be if it were present in a single lump.

A small heap of fine magnesium powder tends to burn rather more slowly than a strip of magnesium ribbon, for example.

The reaction takes place only if the particles in the gas collide with the particles in the solid. Increasing the surface area of the solid increases the chances of collision taking place.

By involving the reaction between magnesium metal and a hydrogen gas. The reaction involves collision between magnesium atoms and hydrogen ions.

$$\mathrm{Mg_{(s)}} + \mathrm{2H^{+}{}_{(g)}} \leftrightarrow \mathrm{MgH_{2}{}_{(s)}}$$

Equation **15** Magnesium Hydride chemical reaction

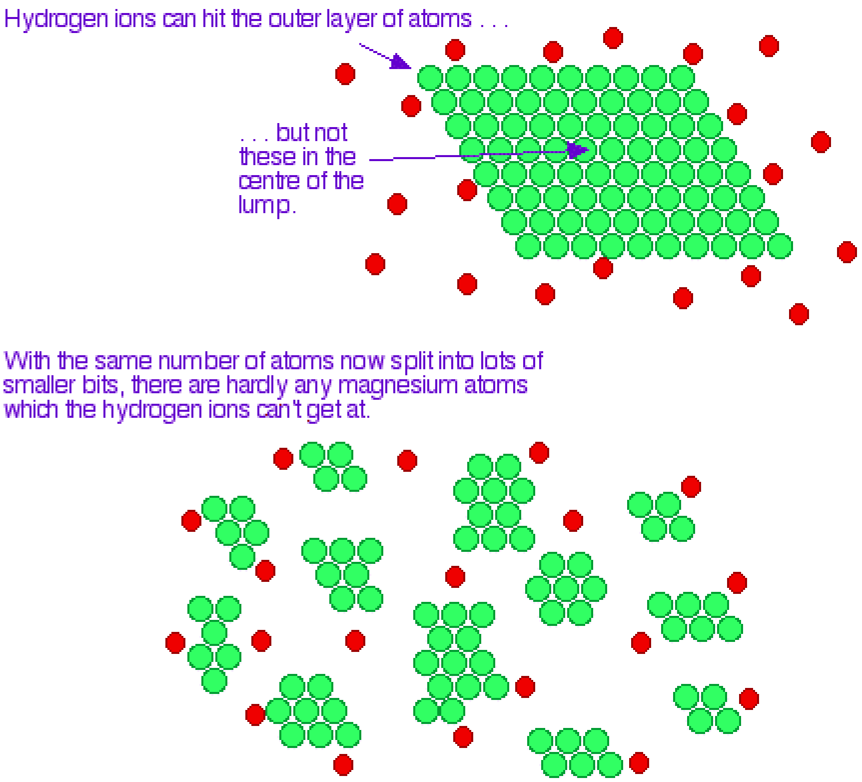


Figure **4.7** Magnesium and Hydrogen collision

Increasing the number of collisions per second; increases the rate of reaction.

4.5 The effect of Concentrations on Reaction Rates

It is described and explained that the way that changing the concentration of a solution affects the rate of a reaction. For many reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction. In a few cases, increasing the concentration of one of the reactants may have little noticeable effect of the rate.

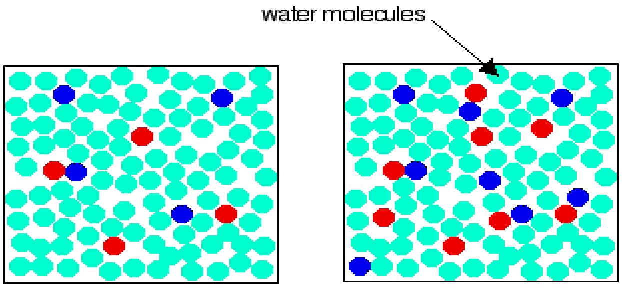
It cannot be assumed that if you double the concentration of one of the reactants that you will double the rate of the reaction. It may happen like that, but the relationship may well be more complicated.

4.5.1 Cases where changing the concentration affects the reaction rate

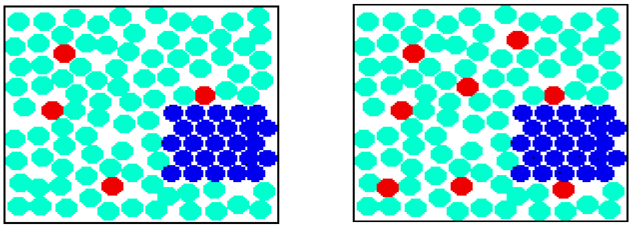
This is the common case, and is easily explained.

- *Collisions involving two particles*

The same argument applies whether the reaction involves collision between two different particles or two of the same particle. In order for any reaction to happen, those particles must first collide. This is true whether both particles are in solution, or whether one is in solution and the other a solid. If the concentration is higher, the chances of collision are greater.



Both reactants in solution



One reactant is a solid

Figure **2.8** Collision of two particles

- *Reactions involving only one particle*

If a reaction only involves a single particle splitting up in some way, then the number of collisions is irrelevant. What matters now is how many of the particles have enough energy to react at any one time.

Suppose that at any one time 1 in a million particles have enough energy to equal or exceed the activation energy. If you had 100 million particles, 100 of them would react. If you had 200 million particles in the same volume, 200 of them would now react. The rate of reaction has doubled by doubling the concentration.

4.5.2 Cases where changing the concentration does not affect the reaction rate

- *Where a catalyst is already working as fast as it can?*

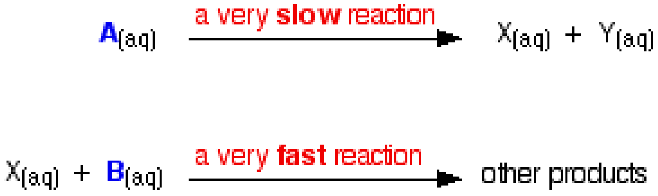
Suppose you are using a small amount of a solid catalyst in a reaction, and a high enough concentration of reactant in solution so that the catalyst surface was totally cluttered up with reacting particles.

Increasing the concentration of the solution even more cannot have any effect because the catalyst is already working at its maximum capacity.

- *In certain multi-step reactions*

Suppose you have a reaction which happens in a series of small steps. These steps are likely to have widely different rates - some fast, some slow.

For example, suppose two reactants A and B react together in these two stages:



Equation **16** Catalyst Reaction

The overall rate of the reaction is going to be governed by how fast A splits up to make X and Y. This is described as the rate determining step of the reaction.

If you increase the concentration of B, which will undoubtedly speed up the second step, but that makes hardly any difference to the overall rate. You can picture the second step as happening so fast already that as soon as any X is formed; it is immediately pounced on by B. That second reaction is already "waiting around" for the first one to happen.

4.6 The effect of Pressure on Reaction Rates

Increasing the pressure on a reaction involving reacting gases increases the rate of reaction. Changing the pressure on a reaction which involves only solids or liquids has no effect on the rate.

For an example, in the manufacture of ammonia by the Haber Process, the rate of reaction between the hydrogen and the nitrogen is increased by the use of very high pressures.

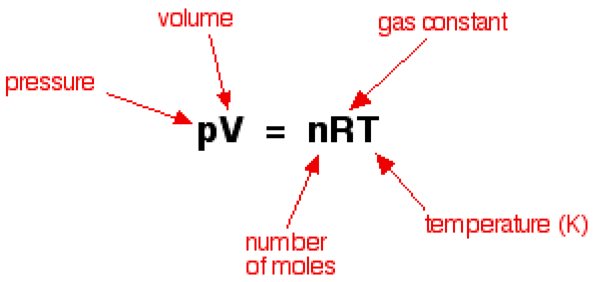
$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

Equation **17**

In fact, the main reason for using high pressures is to improve the percentage of ammonia in the equilibrium mixture, but there is a useful effect on rate of reaction as well.

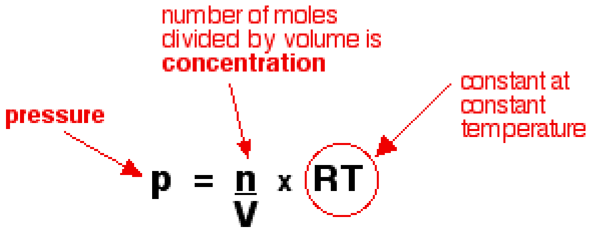
Increasing the pressure of a gas is exactly the same as increasing its concentration. If you have a given mass of gas, the way you increase its pressure is to squeeze it into a smaller volume. If you have the same mass in a smaller volume, then its concentration is higher.

You can also show this relationship mathematically if you have come across the ideal gas equation [44]:



Equation **18** Ideal Gas Equation

Rearranging the equation:



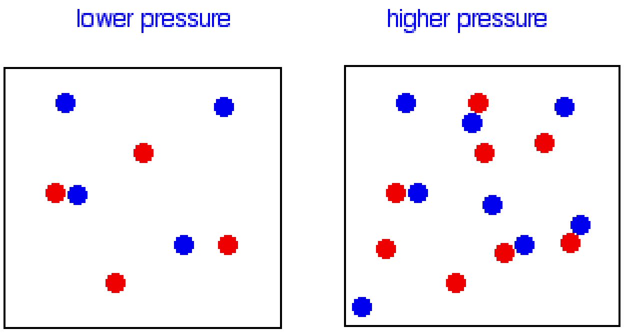
Equation **19** Ideal Gas Equation

Because "RT" is constant as long as the temperature is constant, this shows that the pressure is directly proportional to the concentration. If you double one, you will also double the other.

4.6.1 The effect of increasing the pressure on the reaction rate

- *Collisions involving two particles*

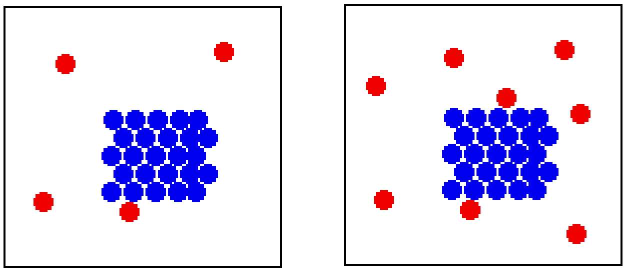
  The same argument applies whether the reaction involves collision between two different particles or two of the same particle. In order for any reaction to happen, those particles must first collide. This is true whether both particles are in the gas state, or whether one is a gas and the other a solid. If the pressure is higher, the chances of collision are greater.



lower pressure

higher pressure

Both reactants are gases



One reactant is a solid

Figure **4.9** Collision of particles at low and high pressures

- *Reactions involving only one particle*

  If a reaction only involves a single particle splitting up in some way, then the number of collisions is irrelevant. What matters now is how many of the particles have enough energy to react at any one time.

4.7 The effect of Temperature on Reaction Rates

As you increase the temperature the rate of reaction increases. As a rough approximation, for many reactions happening at around room temperature, the rate of reaction doubles for every 10°C rise in temperature.

You have to be careful not to take this too literally. It does not apply to all reactions. Even where it is approximately true, it may be that the rate doubles every

9°C or 11°C. The number of degrees needed to double the rate will also change gradually as the temperature increases.

4.7.1 Increasing the collision frequency

Particles can only react when they collide. If you heat a substance, the particles move faster and so collide more frequently. That will speed up the rate of reaction.

It turns out that the frequency of two-particle collisions in gases is proportional to the square root of the Kelvin temperature. If you increase the temperature from 293 K to 303 K (20°C to 30°C), you will increase the collision frequency by a factor of:

$$\sqrt{\frac{303}{293} = 1.017}$$

Equation **20**

That is an increase of 1.7% for a 10° rise. The rate of reaction will probably have doubled for that increase in temperature - in other words, an increase of about 100%. The effect of increasing collision frequency on the rate of the reaction is very minor.

4.7.2 The key importance of Activation Energy

Collisions only result in a reaction if the particles collide with enough energy to get the reaction started. This minimum energy required is called the activation energy for the reaction (Ea). You can mark the position of activation energy on a Maxwell-Boltzmann distribution to get a figure like this:

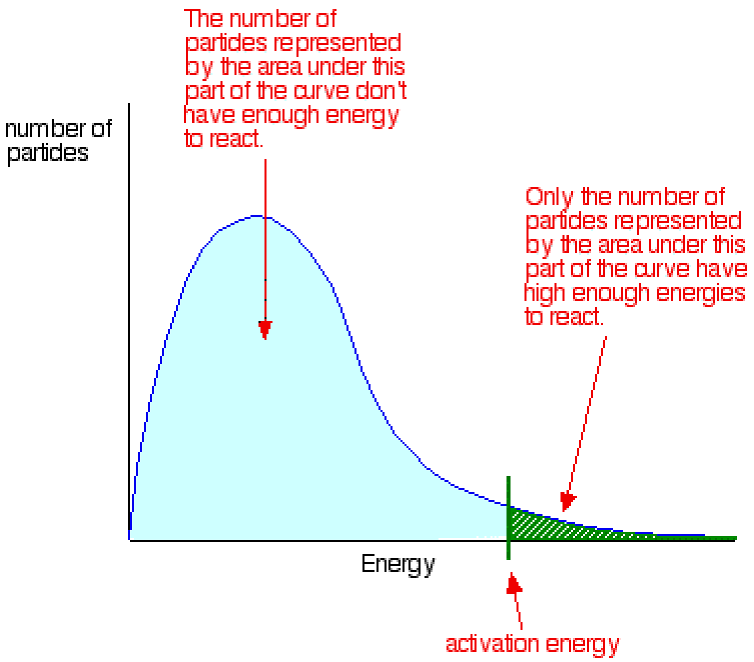


Figure **4.10** Maxwell-Boltzmann distribution

Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority does not have enough energy, and will simply bounce apart.

To speed up the reaction, you need to increase the number of the very energetic particles - those with energies equal to or greater than the activation energy. Increasing the temperature has exactly that effect - it changes the shape of the graph.

In the next diagram, the graph labeled T is at the original temperature. The graph labeled T+t is at a higher temperature.

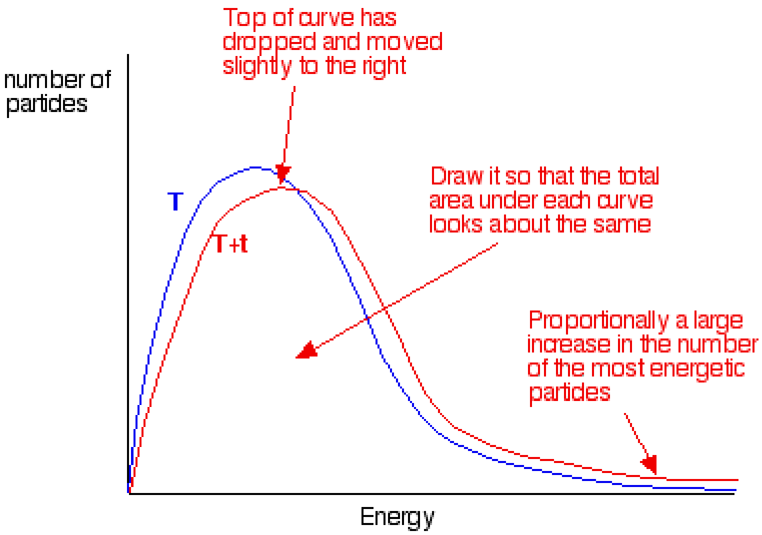


Figure **4.11**a Maxwell-Boltzmann distribution with higher temperature

If you now mark the position of the activation energy, you can see that although the curve has not moved very much overall, there has been such a large increase in the number of the very energetic particles that many more now collide with enough energy to react.

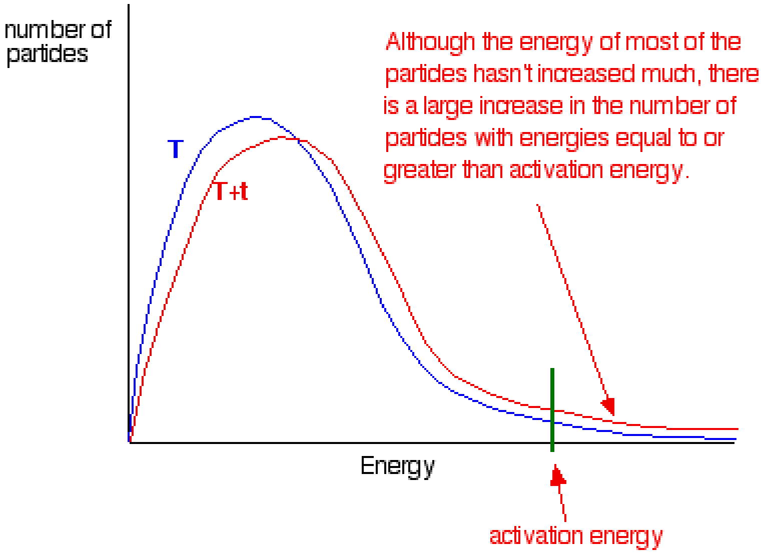


Figure **4.11b** Maxwell-Boltzmann distribution with higher temperature

Remember that the area under a curve gives a count of the number of particles. On the last diagram, the area under the higher temperature curve to the right of the activation energy looks to have at least doubled - therefore at least doubling the rate of the reaction.

4.8 Orders of Reaction and Rate Equations

Changing the concentration of substances taking part in a reaction usually changes the rate of the reaction. A rate equation shows this effect mathematically. Orders of reaction are a part of the rate equation.

4.8.1 Rate Equations

For the purposes of rate equations and orders of reaction, the rate of a reaction is measured in terms of how fast the concentration of one of the reactants is falling. Its units are mol dm^{-3} s^{-1}.

Suppose you had a reaction between two substances A and B. Assume that at least one of them is in a form where it is sensible to measure its concentration, in solution or as a gas.

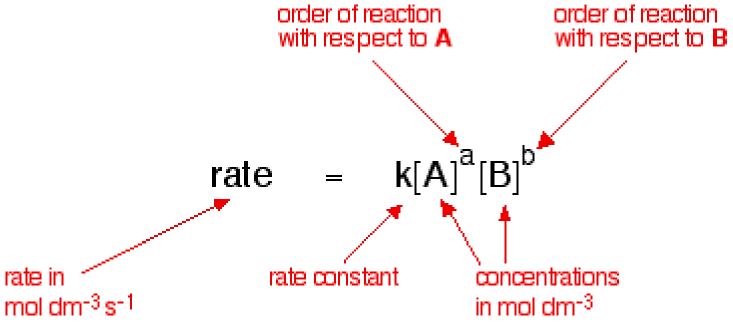
$$\mathbf{A} + \mathbf{B} \longrightarrow \text{products}$$

Equation **21**

For this reaction you could measure the rate of the reaction by finding out how fast the concentration of A was falling per second.

4.8.2 Orders of Reaction

By doing experiments involving a reaction between A and B, you would find that the rate of the reaction was related to the concentrations of A and B in this way:



Equation **22**

This is called the rate equation for the reaction.

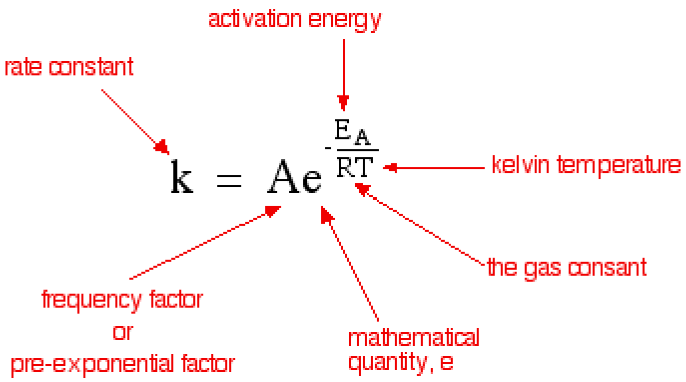
The concentrations of A and B have to be raised to some power to show how they affect the rate of the reaction. These powers are called the orders of reaction with respect to A and B.

If the order of reaction with respect to A is 0 (zero), this means that the concentration of A doesn't affect the rate of reaction. The overall order of the reaction is found by adding up the individual orders. For example, if the reaction is first order with respect to both A and B ($a = 1$ and $b = 1$), the overall order is 2. We call this an overall second order reaction.

4.8.3 Rate Constant

It is only the actual constant if all you are changing is the concentration of the reactants. If you change the temperature or the catalyst, for example, the rate constant changes also.

This is shown mathematically in the Arrhenius equation


activation energy
rate constant
$k = Ae^{-\frac{E_A}{RT}}$
kelvin temperature
the gas consant
frequency factor
or
pre-exponential factor
mathematical
quantity, e

Equation **23**

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the elaboration in this report, it is best said that metal hydrides offer a great opportunity for the improvement of hydrogen storage and transfer. They permit the design of safe, compact and efficient handling equipment. Moreover, as energy carrier and with respect to fossil fuels, hydrogen has advantages with regard to environmental impact and availability. Hydrogen is the only available carbon free fuel and thus can be burnt without the emission of carbon dioxide (CO_2), particles (C), and hydrocarbons (HC).

Magnesium, is chosen to be the metal hydride material used where, in particular it has a high storage capacity (7.6 wt.%) with the benefit of the low cost of the abundantly available magnesium.

For the car model, it is concluded that the hydrogen consumption is almost 5.26 kg for a car of 1200 kg cruising at constant speed of 80 km/h for one hour. Furthermore, the reaction rate for the absorption process of hydrogen by magnesium is calculated by the guide of Vant Hoff and Reaction Rate equations. The rate varied mainly on the temperature change, where as the temperature was increased the rate of reaction increased as well. There are also other conditions that affected the rate of reaction, such as:

- Pressure applied
- Concentration of the reactants (hydrogen and magnesium)

- Surface area of the absorber
- Order of the reaction

5.2 Recommendations

Suggested future work for expansion and continuation will include further researches and literature review on thermodynamics of gaseous and liquid hydrogen storage in metal hydrides.

1. Mechanical grinding can be used to synthesize low and high temperature metal hydride systems. The nano structured materials is beneficial for the hydrogen absorption and desorption kinetics, especially in the case of Mg-based systems where the improvement in kinetics is very significant.

2. Improved kinetics and thermodynamic properties of MgH_2 during hydrogenation/dehydrogenation cycles can be improved by the study of MgH_2-$0.1TiH_2$ material system prepared by ultrahigh-energy-high-pressure mechanical milling.

3. Understanding of the bonding nature of magnesium and hydrogen is essential for improving its hydrogenation/dehydrogenation performance. Therefore, the charge distribution on MgH_2 can be investigated by X-ray diffraction.

4. Predicting the reacted fraction of hydriding/dehydriding (H/D) in powder hydrogen storage materials such as $Mg_{1.95}Ag_{0.05}Ni$ or $LaNiMg_{17}$ alloys.

5. The study of lattice structures of alloys such as $ZrMnFe_{0.7}$, which could be enhanced to improve the hydrogen intake in metal hydrides.

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