The Dissociation of Hydrogen Atom from Neutral and Ion Magnesium Hydride with the Bombardment of Free Hydrogen Atom

Ezman KARABULUT[a] , *Engin YILMAZ[b]*

[a] *Bitlis Eren University, Vocational School of Health Services, 13100 Bitlis, Turkey*

[b]*Bitlis Eren University, Department of Chemistry, 13100 Bitlis, Turkey*

ABSTRACT

In industrial applications, it is essential to provide appropriate experimental conditions to maximize the product. In order to achieve this goal, taking into consideration the appropriate physical conditions such as temperature, pressure, electromagnetic field and evaluating the system as both classical and quantum mechanical provide many advantages. Especially temperature factor is an indispensable parameter for a chemical reaction. Some of these studies are H+ HMg $\square$ H2 + Mg (neutral magnesium) and H+ HMg+ $\square$ H2 + Mg+ (ion magnesium) reactions, examined both quantum mechanically and classically. In order to evaluate this work theoretically with more realistic results, testing the base set function with experimental results comes first of all. In this study, it is seen that the aug-cc-pVQZ base function in the Density Function Theory is more realistic for both systems. The most important factor in the process of separating of the H atom from the Mg atom is the desire of the electron in the HOMO orbital of the separated H atom to interact with the free electron in the Mg atom. Ion magnesium reaction showed to the same state. In the ion reaction, the free Mg+ atom in the product medium has an excited electronic state. This is the result of an ionized magnesium hydride. This requires that the system concerned is an endothermic system. The systems are examined by product state enthalpies (equilibrium constant) and transition state enthalpies (reaction rate constants with transition state theory); after about 600 K temperature, the formation of H2 molecule is was not affected also in both systems. At the same time, the only one of these two reactions is proved by the time dependent quantum method.

1. Introduction

The presence of magnesium hydride has been observed by means of emission radiation from atmosphere of sun and star galaxies (especially from the Cool Stars). The oscillating strength of this radiation representing molecular electronic band transitions is the basis of spectroscopy in subjects such as the existence of molecular species. Roger *et al.* [1] examined the MgH ($A^2\Pi$-$X^2\sum^+$) band system for equilibrium stimulation conditions with a study that controls the density of chemical species. In the study, it was seen that many molecular species could be found in the output plane of a rocket (about 4000 K) used for research purpose. In addition to the MgH molecule, MgO, MgF_2, Mg_2F_4, MgOH and MgF are also determined in certain concentrations. For the MgH molecule, the

* Corresponding author:

E-mail (ezman.fizik@gmail.com)

oscillation strength of the corresponding electronic transition was determined to be about $f = 2.0 \times 10^{-3}$ by transition energy of 2.37 eV. Schadee *et al.* [2] showed that dissociation energy of MgH ground electronic state is 2.49 eV, it has oscillation strength of 8.0×10^{-3}, and if in dissociation energy of 1.85 eV; $f = 3.5 \times 10^{-2}$[1]. The fact that the study is important for astrophysics has made it worth to study both stimulated orbitals and isotopic effects of the Mg atom [3-6]. In a detailed study on this subject, Saxon *et al.* [7] studied the electronic energy states of the molecule. For the ground $X^2\sum^+$ and excited energy states $A^2\Pi$ and $B'~^2\sum^+$ the dissociation energies and the total energies at certain distances were calculated with Self Consistent Field method and were compared with the experimental data. In addition, dipole moment and transition dipole moments (A-X, B'-X and A-B' transitions) were calculated according to the distance between atoms. The vibration quantum energies of the ground and excited states were calculated and also compared with the experimental data. The same authors, in another work [8], computed to the value of oscillation strengths for A-X and B'-X transitions. In case of electronically excited metal atoms with H_2, the mixture of hydrogen gas becomes sensitive to be light. Adams et al. [9] observed the behavior of the stimulated Mg atom against the H_2 molecule. Because of the endothermic behavior of the system they said that the reaction rates could decrease. The saddle point and local minimum geometries were analyzed by MCSCF-CI method. Bernath et al. [10] showed rotational spectrum of MgH by using Fourier transform spectrometer. Also, they discussed factors that can affect to detection of MgH in interstellar galaxy. Breckenridge et al. [11] researched how hydrogen molecule isotope effects distributions of the nascent molecule rotational energy. Liu et al. [12] showed rotational state distribution by depending on temperature and determined reaction pathway for the reaction of Mg (3s3p $^1P_1$) with H_2. Liu and Lin [13] emphasized excited metal atom does not affect the resulting of reaction but effected to inner-distributions of nascent molecule. With this case, the reaction showed to trend of harpoon mechanism features. Generally, the Mg isotope studied has a mass number of 24. This isotope occurs as a result of carbon burning with thermal waves in atmospheric chemistry. Wallace et al. [14] investigated sunspot spectrum data of these three isotopes of Mg. They presented all rotational spectrum belonging to certain vibrational transition for $(B'-X)^2\sum^+$ electronic transition. Liu and Lin [15] showed that Mg(4^1S_0) population is larger than that of Mg(3^1P_1) within pump-probe delay time. In the light of this case, the formation of MgH molecule is effectively encouraged by Mg(4^1S_0) –H_2 reaction rather than one of Mg(3^1P_1). Ou et al. [16] performed Quasi-classical

trajectory calculations on the excited state ($^1A'$) of magnesium atom and the ground state of magnesium hydride to examine angular product distributions for specific product vibrational quantum numbers. Moreover, they showed population distributions depending on scattering angle. The effect of a stimulated metal atom on the formation of metal hydride was the subject of high-probability studies that have recently been center of interest. Liu et al. [17] used Mg ($4~^1S_0$) and Mg ($3~^1D_2$) excited states to occur MgH. Depletion-laser was used to destroy the presence of Mg (3^1P_1) in the reactant channel, as well as to measure MgH in reaction environment. Rotational distributions of the nascent MgH molecule and cross sections depending on temperature were examined. The reaction of excited state Mg with H_2 molecule may compose of unstable MgH_2 complex. This complex structure effects quantum mechanically the formation of MgH, depending on its inner vibration and rotational energy. Hung et al. [18] constructed the improved potential energy surface of Mg (3s3p $^1P_1$) + H_2 ($v=0, N=1$) reaction at CASSCF level for related energy surface, at the same time, they performed quasi-classical trajectory calculations related at N-low and N-high values. From the atmosphere to the earth, after the high heat process, Mg atoms can form metal di-hydrides, MgH_2, is well-known as solid. By melting this solid, it is separated into its constituent components and so the H atom can be used to store energy [19]. Although the formation of MgH_2 molecule occurs in high temperature environment, low temperature environment is needed for its infrared analyzer. For H atom storage, higher energy levels are needed to separate both H atoms from the MgH_2 molecule intermediate complex. The formation of this intermediate complex from the ground reactant molecular system is described by Li et al. [20]. The transition states of all occurrences that may occur after this intermediate complex were determined. These are Mg + H_2, MgH + H and Mg + H + H. In the case of MgH in the ground electronic state, isotopic differences have led to an interesting situation. There are 6 isotopomers with three types of isotopes of magnesium and isotopes of H atom. Shayesteh et al. [21] showed hot-band and fundamental transitions belonging to these isotopomers in R and P branch lines. In another study of Li et al. [22] calculated a new ab initio potential energy surface belonging to Mg+H_2→MgH_2 system. Also, they compared to spectroscopic changes of MgH_2, MgHD and MgD_2 in transition state region with isotopic changes of atom H. In a similar study, Staanum et al. [23]focused on Mg^+ ($3p~^2P_{3/2}$) +HD → MgD^+ + H or MgH^+ + D reactions and examined rare isotopes and short-lived unstable forms. In the case of a counter-reaction of the above-mentioned reaction, Lique et al. [24] created a real potential energy

surface on the formation of MgH_2 in the ground and excited electronic cases. At the same time, they calculated ground and excited potential energies on interaction of Mg (^1S) or Mg(^3P) by H (^2S). MgH (X, A, B') + H (^2S) reaction is examined by taking account into singlet and triplet spin correlations. At the same mechanism that is exoergic, Takayanagi et al. [25] examined the roaming dynamics at certain times of wave function and quantum dynamics calculations at certain rotational and vibrational quantum states. MgH' + H → Mg + H_2 (abstraction mechanism) or MgH +H' (exchange mechanism) with modified potential energy surface are analyzed by Li et al. [26]. They presented that the formation of transition state complex, MgH_2, is created by roaming transition state, but not tight transition one. Tight one causes directly hydrogen abstraction while roaming one indirectly causes highly energetic complex. Population and cross sections are made by quasi-classical trajectory and quantum mechanical methods. In a study made recently [27], Einstein coefficients for A→X and B'→X electronic transitions belonging to ^{24}MgH molecule are examined. In that study are taken account into vibrational quantum numbers (0-11) for ground energy (X $^2\sum^+$) and vibrational quantum numbers (0-3) for the excited (A $^2\prod$) state and (0-4) for the excited (B' $^2\sum^+$) state to calculate Einstein coefficients via rovibrational lines. In the last study, Sanchez et al. [28] showed collisional quantum dynamics of MgH^+ or MgH^- with atom He as depending on temperature. In that study are studied cross sections and reaction rate constants since ionic state-changing reaction changes rotational energy levels.

This work displays the effects of both neutral and ion magnesium to obtain pure H_2 molecule, used as hydrogen fuel. The MgH2 compound is an important storage system for the storage and use of hydrogen gases at any time (desired time). The rest of study is firstly tested by basis set to be used for related systems and secondly reaction rate constants (classical and quantal) and equilibrium constants (classical) are computed. The focus of this study is to show the effect of the last orbital electron of MgH molecule on hydrogen gas formation.

2. Computational Details

In such a study, it is considerable and basis to determine accurate electron affinities of atom and molecular systems. The ground and excited electronic state calculations were solved by means of density function theory. In the energetics of molecular orbitals, self-consistent field (SCF) method was used as convergence method. For the dipole polarization tensor, the Coupled-Perturbed Hartree-Fock (CPHF) equation was used.

However, excited state orbitals were detected by Time-dependent self-consistent field (TD-SCF) method. To this end, configuration interaction singles (CIS) matrix diagonalization was performed [29]. Configuration interaction wave function is specified with the sum of ground and excited orbital wave functions on related spin states. By taking into account the symmetric and antisymmetric states in these calculations, the dissociation energies and equilibrium bond distances can be easily obtained. However, there are some difficulties in determining the behavior of the system in the attractive interaction zone from the equilibrium distance to the dissociation distance. These difficulties are related with adapting to experimental results. Contribution of external effects in experimental environments, the induction and dispersion energies of the system should not be ignored [30-33]. Considering these effects, changes in electrical dipole distributions will also change the oscillation power in electronic transitions [1]. In order to obtain the most accurate electron affinities in the system of Mg and H_2 molecule, the most suitable DFT base set was detected by comparing the ionization energies of the Mg atom and the equilibrium bond distances and the dissociation energies of MgH molecule and excited states in the product channel. In cases where atoms and molecules are very close to each other (where the charges of nuclei have a high effect on electrons), the using of a large number of base functions that allow polarization at high excited energy levels makes the results more precise [34]. The electron affinities of these molecular systems depend the diffuse functions on orbital shifting of the electrons during the dissociation of molecular bonds and the formation of new bonds [35]. The use of the most appropriate base set is possible with highly correlated methods to estimate the limits of the complete basis set [36, 37]. First, the basic functions of ionization energies, including high energy states of the Mg atom, were determined. In ionization cases of internal orbits, the base set of 6-311G ** (3d, p) appears to be more active than the other d and p functions. Up to the third ionization energy, d and p functional conditions and 3d and 3p functions had the same effective mechanism and therefore the values of the augmented sets were more suitable for experimental results because of including only valance polarization (pV) functions. The ionization energies after the second ionization energy of the Mg atom is more than the first two ionization energies. This case indicates to behave like an atom with its noble gas character. The cases described above are shown in more detail in Table 1.

Table 1. The ionization energies of Mg atom. The unit of values is electron volt.

Basis sets	Mg→Mg⁺	Mg⁺→Mg⁺²	Mg⁺²→Mg⁺³	Mg⁺³→Mg⁺⁴
6-31G**(d, p)	7.7287	15.4580	82.4612	120.4153
6-311G** (d, p)	7.7277	15.4631	80.5011	116.2227
6-311G** (2d, p)	"	"	80.5000	116.2218
6-311G** (3d, p)	"	"	**80.4943**	**116.2172**
aug-cc-pVDZ	7.7600	**15.4189**	82.7420	121.1507
aug-cc-pVTZ	7.7279	15.4836	81.9044	119.2218
aug-cc-pVQZ	**7.7260**	15.4885	81.6959	118.5693
Experimental[38]	7.6462	15.0352	80.1437	109.2655

. **Table2.** The dissociation energy, D_e, and equilibrium bond distance (r_e) of MgH (magnesium hydride) on excited and ground states.

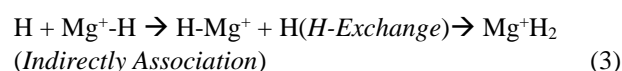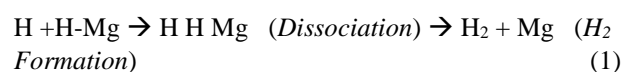| Basis sets	Ground State (X $^2\sum^+$)		1. Excited State (A $^2\prod$)		2.Excited State (B' $^2\sum^+$)	
	D_e (eV)	r_e (Å)	D_e(eV)	r_e(Å)	D_e(eV)	r_e(Å)
6-31G**(d, p)	1.4184	1.7526	1.5244	1.6650	2.0423	1.6856
6-311G** (d, p)	1.4246	1.7473	1.4991	1.6619	2.0549	1.6783
6-311G** (2d, p)	1.4371	1.7432	1.5215	1.6742	3.0945	2.3005
6-311G** (3d, p)	1.4429	1.7411	1.5334	1.6701	3.5603	2.2997
aug-cc-pVDZ	**1.4037**	1.7504	1.4882	**1.6801**	1.5498	1.6704
aug-cc-pVTZ	1.4418	1.7423	1.5368	1.6671	3.0682	2.3029
aug-cc-pVQZ	1.4512	**1.7392**	**1.5471**	1.6644	**0.9562**	**2.3013**
Experimental[7]	1.362	1.730	1.698	1.679	1.296	2.596

All auxiliary functions and basis sets belonging to DFT function group were tested in this study. However, the results that are closest to the experimental values were shared in Table 1. The B3LYP function is the most suitable DFT function for this operation. If Mg, the system is atomic, and the valence electron basis set of the Mg atom is examined up to an energy range from the bond energies to ionization energy, thus it is determined that aug-cc-pVQZ basis set is the most appropriate function. In this study, since the Mg atom is only considered as the behavior of the valence electron, this function is suitable for Mg in the atomic state.
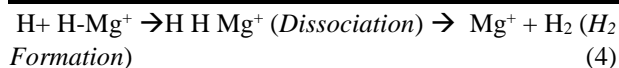
For MgH molecule, ground and 1ˢᵗ and 2ₙₐ dissociation energies and equilibrium bonding distance of excited electronic states are given in Table 2. The molecular system in an experimental environment is under the influence of continuously changing dipole moments. This dipole moment can also induce the dipoles of the surrounding systems. The highest effect of total energy called as dispersion energy, the range is the region between the equilibrium bond distance and the dissociation distance and these energies vary as depending on the polarity of the molecule [31].

$$Dispersion\ Energy = -\frac{3\alpha^2 E_i}{4(4\pi\varepsilon)^2 r^6}$$

Here α is polarizability and E_i is ionization energy. The dispersion energy contributes greatly to the long-distance attractive interaction regions. Therefore, for the MgH molecule, large deviations may occur in the region of the dissociation energy, especially in the excited energies. On the contrary, in the short-range impulsive energy region, there is a situation that reduces the densities of the electron. This is also ideal for determining the useful basis function. In these ground and excited states, instead of referring to the dissociation energy, it is more convenient to use the basis function which is close to the equilibrium bond distance that is experimental. In this study, the most suitable basis set is considered as aug-cc-pVQZ for MgH molecule. Already, several studies [39, 40] have supported the use of this base set for these molecular groups.

For the Mg-H-H system, so far, the base functions that should be used are discussed. In the following part of the study, the effects of linear interaction of H + MgH reaction on both neutral and ionic magnesium atoms will be discussed.

H +H-Mg → H H Mg   (*Dissociation*) → H₂ + Mg   (*H₂ Formation*)   (1)

H+ Mg-H → H-Mg-H   (*Directly Association*)   (2)

H + Mg⁺-H → H-Mg⁺ + H(*H-Exchange*)→ Mg⁺H₂ (*Indirectly Association*)   (3)

H+ H-Mg$^+$ →H H Mg$^+$ (*Dissociation*) → Mg$^+$ + H$_2$ (*H$_2$ Formation*)   (4)

Reaction (1) represents the case when the H atom approaches the MgH molecule by the H atom. System's most stable spin state is generated by Triplet state. Before the H$_2$ molecule forms in the system, the H atom is separated from the MgH molecule. In reaction (2), the system performs its most stable formation in the singlet state and directly forms the MgH$_2$ molecule. In reactions (3) and (4), the system is in a doublet spin state. In reaction (3), after H-exchange occurs, MgH$_2$ is formed. In reaction (4), H$_2$ molecule is formed after separation of H atom from MgH. From these reactions only reactions (1) and (4) are discussed to examine, because of strongly allowing the formation of the H$_2$ molecule. In these reactions, the Morse curves of the most stable energy states of the approaching H atom at 0 and 180 degrees are given in Figure1.

In all of reactions in Figure 1, the H atom approaches the MgH molecule. In the case of reaction (1), it is the same as situation that two charges having the same spin state come close to each other. In such a case the barrier is formed. The most effective electrons in the barrier region are electrons of H atoms until a stable H$_2$ is formed. After a stable H$_2$ molecule occurs, active electronic case (first affected by external forces) is on magnesium. If in the reaction (4) that is another case which supports H$_2$ formation, active electrons are also collected on H$_2$ molecule as well as Mg ion. Global potential energy surfaces are used to obtain reaction rate constants with time-dependent Schrödinger equation in three dimensions for the reactions occurring H$_2$. One for neutral reactions (reaction (1) and (2)) is used multi-reference configuration interaction method with the Davidson correction (icMRCI+Q) and the cc-pVnZ (n=3, 4, and 5) basis sets in Ref. 26 and if for the other ones (reaction (3) and (4)) *ab initio* calculations are performed on the VQZ basis set (see Ref. 40).

In the Neutral Mg system, the reason of the barrier height formed during the approaching H atom is the electron of the H atom that wants to leave the Mg atom and that tends to interact with the free electron in the Mg atom. This means that the leaving H atom has the HOMO (High Occupied Molecular Orbital) energy towards the Mg atom. After exceeded the barrier, no electrons are seen in the HOMO. The same case is not in the ion Mg system. No barrier occurs due to an ionized Mg atom. Therefore, the reaction rate is also expected to be higher. Although the oscillator strength is low in this barrier in the neutral reaction, it is the region with the lowest energy electron transition. (459nm).

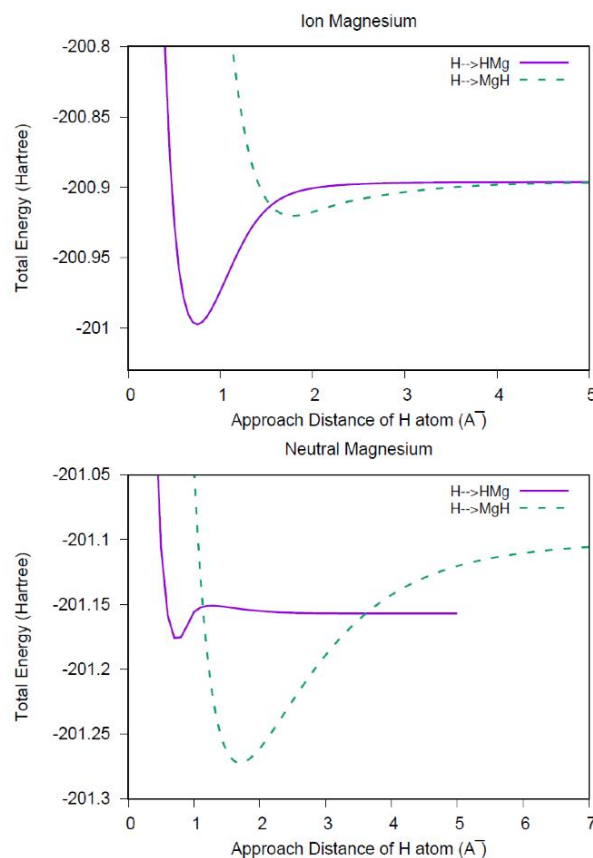However, in the case of ion Mg, the electronic transitions emitted are in the UV region.

Figure 1. Potential energy surfaces of the H atom approaching to MgH molecule at 0^0 and 180^0 for neutral (the lower part) and ion (the upper part) magnesium atoms. 0 degree is the approaching of H atom by Mg and is shown with dashed lines. 180 degrees is the approaching of H atom by H atom to MgH molecule and it is indicated by a straight line. The latter supports H$_2$ formation.

3. Classıcal Reaction Rate Constants (Transition State Theory) and Equilibrium constants

The reaction rate constant can be calculated with the transition state theory based on the enthalpy changes in the reactants and transition states of a reaction. At the same time, once considering the entropy and enthalpy in the product and reactant regions, equilibrium constants which are exponentially inversely proportional to the reaction rate constant can be obtained. The reaction rate constant refers to the state of the reaction in the desired direction (in one direction). The equilibrium constant is considered with the reaction and its reverse. The equilibrium constant is a dimensionless constant.

3.1. Transition State Theory

In this section only the changes of enthalpies in the transition state and the reactants are important. Reaction

rate constants obtained by depending on electronic and thermal enthalpies values are obtained by using DFT-B3LYP method [41, 42] and aug-cc-pVQZ basis set at geometries determining reactant and transition regions. These values are given in Table 3. Also, transition geometric states for neutral and ion magnesium are showed in Figure2.

Ion Magnesium Reaction

θ=46.88

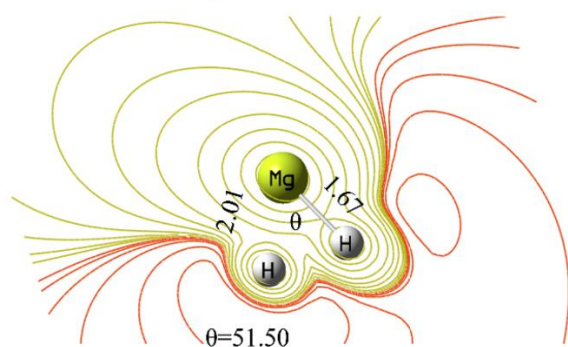## Neutral Magnesium Reaction

θ=51.50
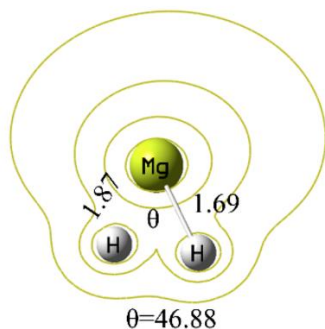
Figure2. The geometries of Transition states for neutral and ion magnesium. The atomic distances on the picture are in angstrom units. Angles are degrees.

For neutral and ion magnesium, Figure 2 emphasizes the geometric distances and angle values of the transition state of MgH_2. In the neutral mg system on the right side of Figure 2, the electrostatic potential energy region caused by the free electron in the Mg atom is seen. At the same time, this electron prevents the decomposition of the H atom at MgH. So the MgH molecule forms an energy barrier around itself. This barrier is between the free H atom and the H atom bound to Mg. This is not the case for a free H atom from the Mg side. Because it has an electron tending to bond at the Mg atom.

The excited state (^{3}p) of Mg at Table 3 was not needed since it has been in product channel. The reverse of the present ion reaction was carried out experimentally by means of induced excitation reaction with an electron bombardment. However, when the ion reaction is considered in the present form, it is an endothermic reaction that requires external energy. Reaction rate constants were calculated by the transition state theory, which takes advantage of two stable states of a system moving from reactants to activated complex region. According to this theory, the system is assumed to be stable at a very small distance in the transition state region. Experimentally, let us assume that the MgH reactant molecule is numerous in the system, the formation of H_2 occurs as much as the increasing H atom. Vice versa, when the H atom is too much, the increasing MgH molecule will cause to increase the reaction products at the same rate.

Table.3. Reaction rate constants and electronic and thermal enthalpies depending on temperature for reactant and transition states. Since the H atom is neutral in the reactant state, it was not worth mentioning additionally in the part of the ion reaction parameters. The value is the same in both cases.

	Neutral Reaction				Ion Reaction		
	Enthalpies (Hartree)			Rate Constants ($cm^3mole^{-1}s^{-1}$)	Enthalpies (Hartree)		Rate Constants ($cm^3mole^{-1}s^{-1}$)
Temp.(^{0}K)	H	MgH	TS	k(T)	MgH^+	TS	k(T)
100	-0.5016	-200.650	-201.135	9.47×10^{-33}	-200.388	-200.895	2.00×10^{-3}
298.15	-0.5000	-200.648	-201.133	40.6×10^{-18}	-200.386	-200.893	2.73×10^{-7}
400	-0.4992	-200.646	-201.131	4.56×10^{-15}	-200.385	-200.891	0.93×10^{-7}
500	-0.4984	-200.645	-201.130	0.72×10^{-13}	-200.384	-200.890	0.51×10^{-7}
600	-0.4976	-200.644	-201.128	0.46×10^{-12}	-200..383	-200.888	3.50×10^{-8}
700	-0.4968	-200.643	-201.127	1.83×10^{-12}	-200.381	-200.887	2.68×10^{-8}
800	-0.4960	-200.641	-201.125	5.16×10^{-12}	-200.380	-200.885	2.21×10^{-8}
900	-0.4952	-200.640	-201.123	11.56×10^{-12}	-200.379	-200.883	1.92×10^{-8}
1000	-0.4944	-200.639	-201.122	22.19×10^{-12}	-200.378	-200.882	1.70×10^{-8}

For this reason, the system considered is known as 1st degree. Reaction rate equation is written as

$$\frac{d\ (Product)}{dt} = k\ [Reaktants] \tag{5}$$

here k is reaction rate constant. Activated complexes in the system are MgH_2 and MgH_2^+. Equilibrium constant between reactants and activated complex is

$$K_C = \frac{[MgH2]/c}{[H]/c[MgH]/c} \tag{6}$$

where c is standard case concentration and is known as 1.00 mole/dm^3. however, the equilibrium constant is the equilibrium constant which is dependent on molarity. This is not the equilibrium constant mentioned in title of Section 3. it will be mentioned at the end of this section. Once considered a transition state that is suitable for translation motion in one dimension and that exceeds the barrier, by using the Maxwell-Boltzmann distribution in one dimension, the reaction rate constant equation is obtained as follows. Reaction rate constants in Table 3 are calculated [43] by

$$k(T) = \frac{k_B T}{hc}\ e^{-\Delta G/RT} \tag{7}$$

where k_B is Boltzmann constant, R is ideal gas constant and T is temperature. ΔG is electronic and thermal enthalpies between reactants and transition state. That is, it is also called as free activation energy. These rate values do not depend on the masses of atoms in system. This is known as the rate of product formation. Reaction rate constant are proportional to concentration of reactants. Molhave et. al. [44] showed experimentally the formations of MgH^+ and its isotope below temperature of 1K because of laser cooled Mg^+ ions. Theoretically, there is only one MgH2 molecule in the system. So it will be necessary to reassess the term (1/c) in equation (7). It is necessary to determine the concentration for a single molecular system. In order to determine the concentration, firstly the molar volumes of the neutral and ion states in the transition states in Figure 2 are obtained. The molar volumes obtained using the same base functions are the same for ion and neutral and have a value of 25.704 cm^3/mol. Total molar masses of two H atoms and 1 Mg atoms is 26.327 g / mol. Using this data, the transition state gas density is 1.023 g/cm^3 (It is known that the density of MgH_2 in crystal form is 1.45 g/cm^3). If 6.02×10^{23} MgH_2 molecules in 1 mole is found in the volume of 25.704 cm^3/mol, 1 MgH_2 molecule is found in volume of 4.269×10^{-23} cm^3/molecule. This value is the reverse of the volume of the MgH_2 molecular system which reaches the transition state region and thus contributes to the formation

of the product molecule. That is 1/c. When this coefficient is also taken into account, the unit of reaction rate constant coefficient is cm^3/(molecule.s). The reaction rate constant results obtained as classically are given in Table 3.

Conical Variational Theory and Improved Conical Variational Theory were studied to calculate thermal rate constants at atom-molecule collisions. At low temperature regions, it was seen that these thermal constants have fairly low values. These reactions in three dimensions are $I+H_2$, $O+H_2$, Cl+HD and $Cl+H_2$[45, 46]. Reaction rate constants for neutral magnesium is also small enough to indicate that the reaction is not possible.

3.2. Equilibrium Constants

The reaction rate constant the above-mentioned is calculated by the transition state theory. However, the equilibrium constant is calculated by considering enthalpies and entropies between the product and the reactants. In exponential expression in Equation (7), the exponential part is known as the equilibrium constant (K). Increased equilibrium constant indicates a decrease in reaction rate.

$$K = e^{-\Delta G/RT} \tag{8}$$

Table 4. shows the temperature-dependent equilibrium constants using the differences in Gibbs free energies in the product and reactant channels for ion and neutral magnesium reactions.

Usually in gas phase reactions, entropy does not affect the results of Gibbs free energy. However, it is a highly effective factor at high temperatures. In this study, it has an effect of less than 1% at 100 K, while it is around 11% at 1000K. The negative of enthalpy denotes exothermic reaction while positive of enthalpy indicates endothermic reaction. Therefore, especially in protonation studies, there are differences depending on the temperature range examined [47-50]. For reaction, here = product- reactant. The increase of the calculated equilibrium constant indicates that the resulting species are stable. If equilibrium constant is not stable, reaction runs in the opposite direction. For these reasons theoretical studies are important to predict the direction of the reaction. Also it important to predict what will happen at different temperatures without experiment. In this study, very small equilibrium constant values belong to endothermic ion reaction with 1.8 eV barrier. This reaction is more suitable in the opposite direction.

Table 4. ΔH (enthalpies in unit of Hartree), ΔS (entropies in unit of Cal/Mol.K), ΔG (free Gibbs energy in unit of Kcal/Mol) and K (Equilibrium constant, which hasn't any unit) related on product and reactant channel. Here value of K is calculated by Equation (8).

Temp.(^{0}K)	Neutral Mg System				Ion Mg system			
	ΔH	ΔS	ΔG	K	ΔH	ΔS	ΔG	K
100	-0.115695	-6.87	-71.91	2.51×10^{69}	0.080787	-3.91	51.08	4.99×10^{-50}
298.15	-0.115705	-6.88	-70.55	6.98×10^{22}	0.080788	-3.92	51.86	1.60×10^{-17}
400	-0.115730	-6.93	-69.84	7.0×10^{16}	0.080771	-3.94	52.25	2.49×10^{-13}
500	-0.115798	-7.02	-69.15	2.2×10^{13}	0.080728	-4.00	52.65	6.87×10^{-11}
600	-0.115903	-7.14	-68.44	1.0×10^{11}	0.080655	-4.08	53.06	2.92×10^{-9}
700	-0.116041	-7.28	-67.72	2.1×10^{9}	0.080550	-4.18	53.47	4.2×10^{-8}
800	-0.116207	-7.41	-66.99	1.1×10^{8}	0.080416	-4.29	53.90	3.1×10^{-7}
900	-0.116392	-7.55	-66.24	1.2×10^{7}	0.080262	-4.41	54.33	1.5×10^{-6}
1000	-0.116587	-7.68	-65.47	2.0×10^{6}	0.080094	-4.52	54.78	5.1×10^{-6}

4. Reaction Rate constants (Quantum Mechanically)

To calculate reaction rate constants for atom-diatom reactions, there are many of works in literature [51-53]. These works have solved time-dependent Schrödinger equation by means of Real Wave Packet, using specific initial quantum states (vibrational and rotational quantum states). The inner quantum states corresponding to this study is lowest inner quantum numbers (v=0, j=0). If product channel, it is the sum of all available inner quantum states. In another words, these reactions are H + MgH (v=0, j=0)→ H$_2$ ($\sum$v, j) +Mg (neutral reaction) and H + HMg$^+$(v=0,j=0) → H$_2$($\sum$v, j) + Mg$^+$ (ion reaction). Total angular momentum quantum number in these calculations *J*, is zero. Wave packet used in calculations is the normalized amplitude depending on the energy of Gaussian wave packet. Reaction probabilities are obtained with solving of time-dependent Schrödinger equation. To be able to perform total cross-section calculations, the contributions of all total angular momentum must be taken into account. To use the j-shifting approach as a simple approach, due to the potential energy structure of the subject reaction, does not constitute a significant margin of error in the total cross section. The assumption underlying the j-shifting approach is that the reaction takes place in the transition state and the rotation energy E_J of the three atomic molecular systems is not enough to overcome the barrier energy of the reaction. The advantage of this approach is that it only needs to calculate the reaction possibilities for the J = 0 state. For J>0 states partial reaction probabilities are obtained by

$$P_{vj}^{J}(E_{Col}) = P_{vj}^{J=0}(E_{Col} - E_J^*) \qquad (9)$$

where value of E_J^* (that is, the shifted energy with contribution of *J*) is calculated by

$$E_J^* = \frac{\hbar^2}{2\mu_{BC}r^2}J(J+1) \qquad (10)$$

The total cross sections are summed over the partial total angular momentum quantum states and are obtained by the following formula

$$\sigma_{v,j}^{K}(E) = \frac{\pi}{k_{v,j}^2}\sum_{J}^{Jmax}(2J+1)P_{v,j}^{JK}(E) \qquad (11)$$

Rate constants for specific initial states are calculated by a Maxwell-Boltzmann distribution over the collision energy [54].

$$k_{vj}(T) = \left(\frac{8}{\pi\mu_Rk^3T^3}\right)^{\frac{1}{2}}\int_0^{\infty}dE_{Col}E_{col}e^{-\frac{E_{Col}}{kT}}\sigma_{vj}(E_{col}) \qquad (12)$$

Quantum mechanically reaction rate constants are only calculated for neutral Mg system. In ion Mg system used the potential energy surface of Ref. 40, the obtained results are not converged on a single processor. For this reason, it is not included to this study. The detailed quantum calculation of the ion Mg system can be done using the parallel processor calculation. Neutral Mg reaction has both classical and quantum mechanical results. Classical ones are calculated by DFT method on B3LYP basis set and quantum one is calculated by Real Wave Packet method on potential energy surface in Ref. 26. In transition state of the system, R is 3.36 a.u. (distance of coming H atom to Mg atom), r=3.44 a.u. (distance of MgH molecule) and angle is 55.4 degree on potential energy surface of Ref. 26, while R is 3.80 a.u., r is 3.15 a.u. and ve 51.5 degree on DFT. In cross-sections calculations, transition distance (distance of coming H atom to center of mass of MgH molecule) is specified as 2.94 a.u. Figure 3 shows reaction rate constants both classical and quantal and equilibrium constants that is classical for neutral Mg system. Reaction rate constants increase with temperature. Transition state theory has highly compatible results with quantum mechanical results at high temperatures while it has not at low temperatures. The equilibrium constant indicates that the reaction requires higher temperatures to reach an equilibrium. The fact that the equilibrium constants give an exponentially inversely

proportional results to the reaction rate constants obtained by the transition state theory shows that an appropriate transition state is selected for this reaction.
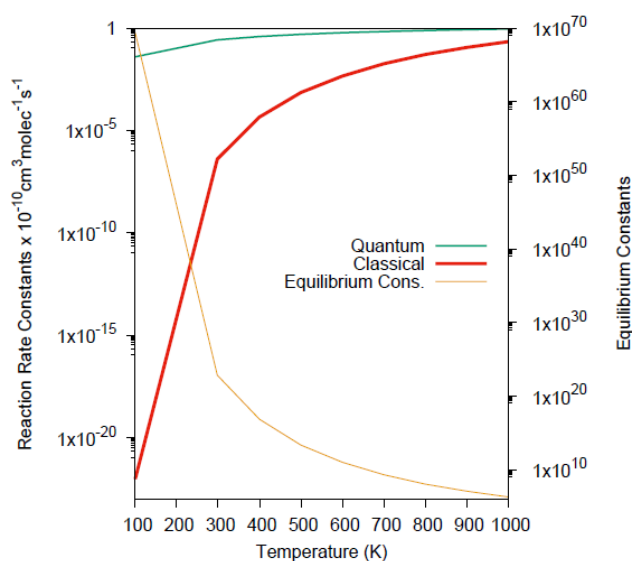

Figure 3. Reaction Rate constants and Equilibrium Constants for Neutral Mg system.

Figure 4 shows reaction rate constants and equilibrium constants for ion Mg system. Because of convergence problem, it has only classical results. According to Figure 4, in the temperature range examined, tending of ion reaction to reach thermal equilibrium is better than the neutral system. It has a very high reaction rate at low temperatures.
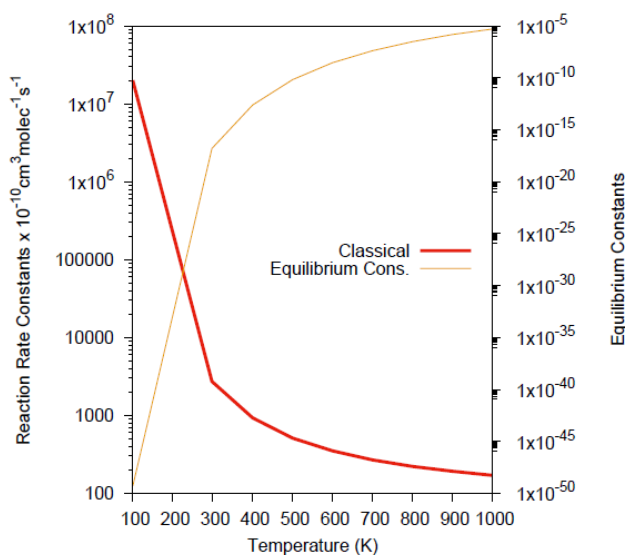

Figure 4. Reaction Rate Constants and Equilibrium Constants for Ion Mg System.

In Ref. 44 is also experimentally showed to be an effective reaction rate. When the neutral and ion states are compared with each other, it is seen that the ion reaction achieves thermal equilibrium at lower temperatures, according to the curve of equilibrium constant, although it is endothermic.

5. Conclusion

This work shows the effect of ion and neutral cases of a reaction on reaction rate constants. If reaction has a barrier and there is a change in its barrier after ionization, electrostatic state of the system changes. This change effects many of dynamical process, as well as enthalpy states. At the same time, this work is a study showing that excited alkali metals have the high efficiency at low temperatures. The accuracy of the transition state is tested by that reaction rate constants compare with equilibrium constants. In many studies using enthalpy and entropy, information about reaction rate constants can be obtained by the help of this study. the dispersion energy-intensive ranges are where the Centrifugal barrier is effective. Therefore, making calculations in certain total angular momentum states can offer a more effective reaction rate constant. However, in the high temperature region, classical and quantum mechanical results are in good agreement with each other. When compared with the neutral reaction, the ionic reaction enters the thermal equilibrium at a lower temperature.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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