

Multitude of elementary chemical reactions between the first two elements in the periodic table: Topic for pedagogic discussion and contemporary research

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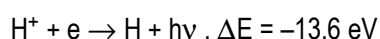
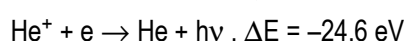
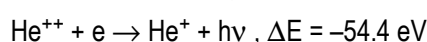
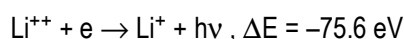
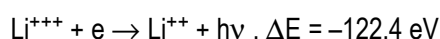
ABSTRACT

The first two elements in the periodic table seem to have been formed in the early universe, in the order, helium and hydrogen. Helium considered a rare gas on earth was nearly 10% in abundance when compared to that of the most abundant element hydrogen. Interestingly, the first chemical reaction seems to have occurred between He and H⁺ to yield HeH⁺, which in turn reacted with H to yield H₂⁺. The formation of H₂⁺ seems to have paved one of the pathways to form H₂. HeH⁺ could react with H₂ to form He and H₃⁺, the first triatomic species to be formed. It is shown in this article how rich chemistry occurred between helium and hydrogen in the early universe and how they could be the topics for pedagogic discussion as well as fundamental research.

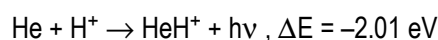
1. Introduction

In the beginning of my college days, I learned that there were inert (or noble) gases and that their atoms had a stable electronic configuration and that they did not react with other elements in the periodic table. Subsequently, I learned that they were not so inert and that they reacted with some elements like oxygen and fluorine. They are called rare gases in current textbooks. While they may be rare on earth, the lightest of them, helium was not so rare in the early universe. Even today, a lot of it is buried deep under the earth and it comes out along with other natural gases.

From what we understand from cosmologists about the early universe, helium was the first element to be formed in the beginning of the chemical epoch, when the temperature (T) was of the order of 3000 K [1]. Hydrogen and helium nuclei were present in the ratio of 1: 0.1 and there was a bit of lithium (of the order of 10⁻¹⁰). Because of the low particle density in the early universe, collisions were unlikely and there were no third bodies available. The only mechanism available for the atoms to be formed was the recombination. Energetics dictated that neutral helium atoms were formed first, followed by hydrogen and lithium atoms:

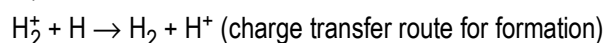


It was only natural that the neutral He atom would react readily with the abundant protons to form HeH⁺, the first diatomic molecule to be formed in the early universe [2]:



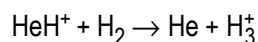
This in turn, led to a variety of other reactions:

HeH⁺ + H → H₂⁺ + He (the first exchange reaction to take place)

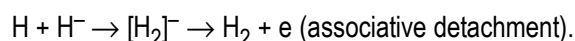


In other words, He and H⁺ would undergo reactions and get regenerated while forming H₂⁺ and H₂. That would be an auto-catalysis or a feedback mechanism.

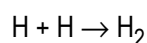
It appears that HeH⁺ could react with H₂ to form H₃⁺, the first triatomic species to be formed in the early universe [3]:



Although the route mentioned above for the formation of H₂ became available, it appears that H₂ was formed by a faster route that has its origin in the formation of H⁻ [1]:



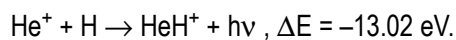
It is worth pointing out that the commonly envisaged mechanism for the formation of H₂



could not take place in the early universe because the dipolar mechanism of radiative association was not available and there was no third body to facilitate the process either.

Although HeH⁺ was detected in a mass spectrograph in 1925 in the laboratory [4], it was only in 2019 that it was detected in

the planetary nebula (PN) NGC 7027 [5]. Interestingly, the preferred mechanism for the formation of HeH^+ in PNe seems to be



Although HeH_2^+ was detected in the same mass spectrograph as HeH^+ , it has not been detected in interstellar media so far.

He^+ could, in principle, react readily with H_2 and form $\text{HeH}^+ + \text{H}$ (hydrogen atom transfer) and/or $\text{He} + \text{H}_2^+$ (charge transfer). In practice, however, that does not seem to happen because of orbital symmetry considerations [6]. Experimental evidence suggests the formation of $\text{He} + \text{H} + \text{H}^+$ (dissociative charge transfer). It is worth adding that these reactions do not take place in the ground electronic state of HeH_2^+ and would involve non-adiabatic interactions which take us beyond the Born-Oppenheimer approximation [7].

2. Summary and conclusion

It has been pointed out that helium was the first neutral atom to be formed in the early universe and that it reacted readily with protons. Helium was neither rare nor inert. The first formed diatomic species HeH^+ was perhaps responsible for the formation of the first triatomic species H_3^+ . There is a rich chemistry involving He , H , He^+ , He^{++} , H^+ , H_2 , H_2^+ and H_3^+ waiting to be explored.

3. Pedagogical aspects

How to compute rates of recombination and (dipole) radiative association?

How to compute rates of elementary chemical reactions?

What was the consequence of autocatalysis by He and H^+ in the early universe?

How does the conservation of orbital symmetry govern the feasibility of certain chemical reactions?

How to compute potential energy curves for diatomic molecules and potential energy surfaces for larger systems?

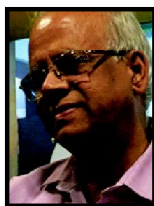
How to compute nonadiabatic coupling terms between different adiabatic potential energy curves and surfaces and how to carry out quantum dynamics on a multi-sheeted potential energy surface?

Conflict of interest

none

References

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Dr. N. Sathyamurthy, Honorary Professor at the Indian Institute of Science Education and Research (IISER) Mohali, retired as an Institute Chair Professor of Chemistry from the Indian Institute of Technology Kanpur. An author/coauthor of more than 200 research papers, he works in the areas of chemical dynamics, nonadiabatic interactions and atomic and molecular clusters in free state as well as under confined conditions. He received the S. S. Bhatnagar Prize in Chemical Sciences and is a Fellow of the Indian Academy of Sciences, Bengaluru, Indian National Science Academy, New Delhi and The World Academy of Sciences, Trieste, Italy.

