Atom tunneling in chemistry

While macroscopic objects from everyday life follow the classical laws of physics, microscopic objects obey the laws of quantum mechanics. These quantum objects, such as light (photons), electrons, and atoms, show characteristics of particles as well as waves and therefore display unexpected behavior.

One example is the tunnel effect which allows particles to surpass barriers with a higher potential energy than the total energy of the system. This would be forbidden in classical physics, according to Newtonian mechanics.

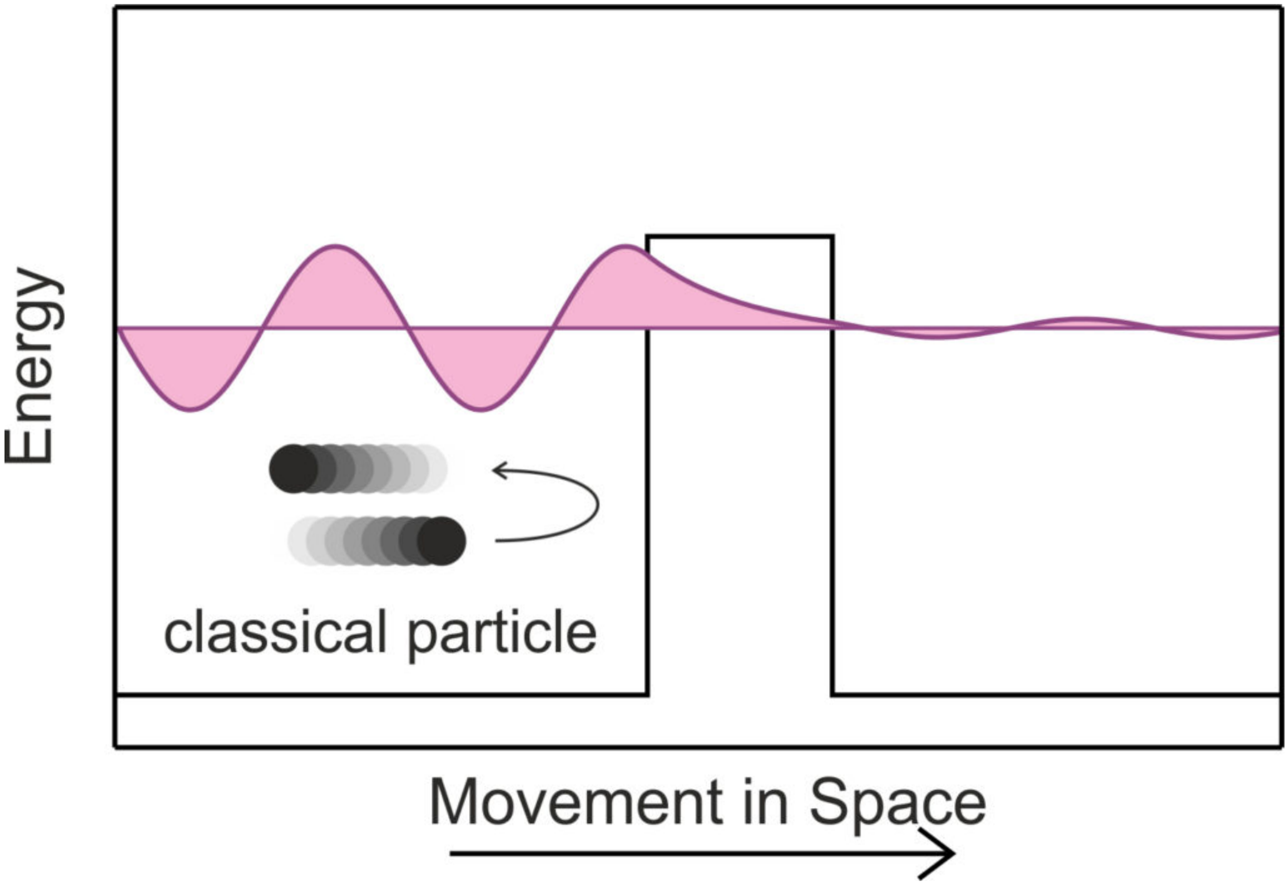

Fig. 1. Classical particles are reflected by a barrier if the potential energy is too high. The quantum nature of small objects permits a penetration of the barrier which can, in the case of atoms and molecules, lead to chemical reactivity.

Atoms in molecules behave like quantum objects, too, and can tunnel through the activation barrieres of chemical reactions. Even if the energy, i.e. temperature, is too low to overcome the activation energy, reactions can take place. This happens when the barrier is narrow and high or if the temperature is particularly low. Chemical reactions can therefore happen even in the interstellar medium where the temperature is as low as just a few Kelvin.

Figure 2 shows the temperature dependence of the rate of a chemical reaction involving tunneling: at higher temperature (left), in most cases room temperature, the logarithmic reaction rate behaves classically and decreases linearly with decreasing temperature. At moderate temperature, the Arrhenius plot displays a curvature with a diminished slope, which is becomming nearly zero at very low temperatures. Thus, the reaction rate stays constant from a particular temperature on, because tunneling dominates the reaction.

In addition to the shape of the potential energy barrier, the probability of a particle tunneling through a barrier is also mass-dependent: lighter particles possess a more pronounced quantum character and tunnel is more likely.

This leads to the experimental finding that a substitution of protium (the light hydrogen isotope) by deuterium (heavy hydrogen) decreases the reaction rates when tunneling is involved. The ratio between the reaction rates of the light and heavy isotope is called kinetic isotope effect and is therefore an experimental measure of the impact of tunneling.

Some reactions can be even be suppressed when the hydrogen atoms are exchanged by deuterium atoms, indicating that tunneling is essential for the reaction mechanism.

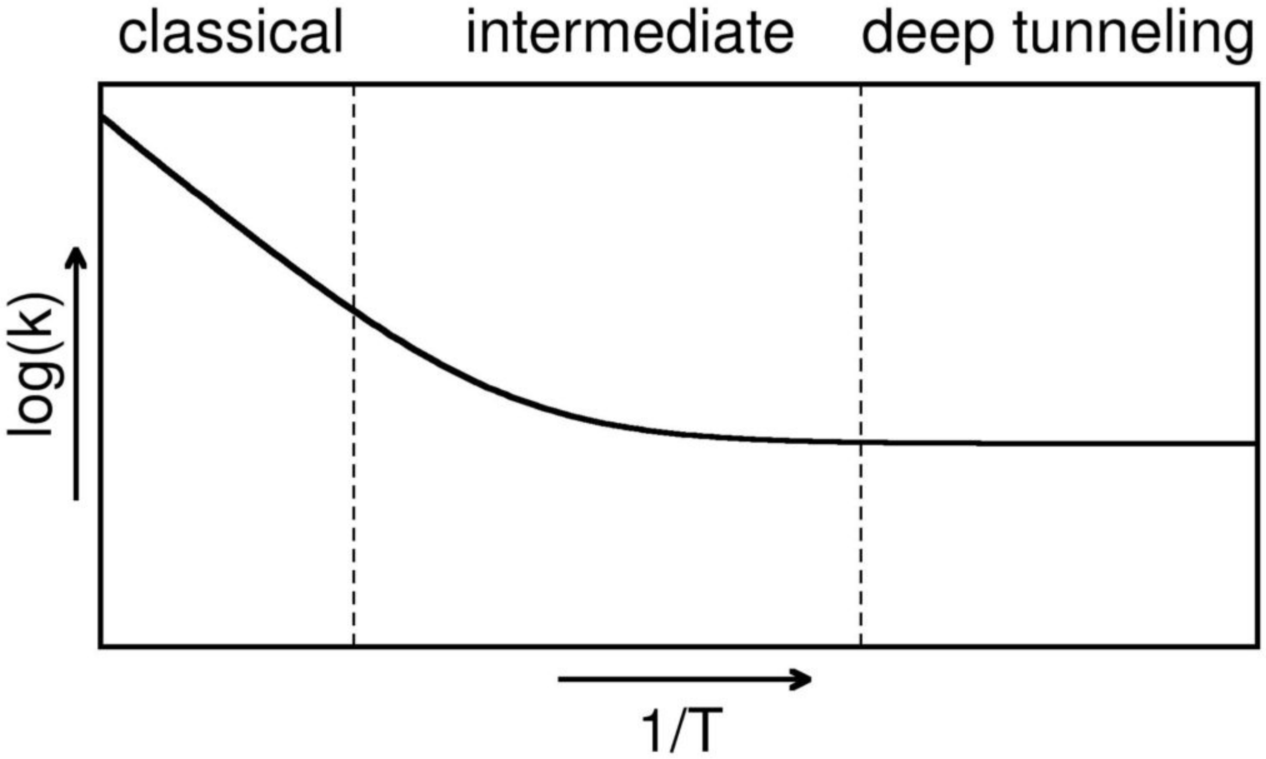

Fig. 2. Dependence of the logarithmic reaction rate constant against the inverse temperature, called an Arrhenius plot.

One interesting finding is the deuterium enrichment in small organic molecules in the interstellar medium, such as methanol or formaldehyde. A partially deuterated molecule can react with a radical species and a hydrogen atom can be abstracted. Since this process is enhanced by tunneling, a protium atom is more likely to be abstracted than a deuterium atom.

As this happens repeatedly over astronomic time scales, the amount of chemically bound deuterium increases.

In our review article we give an overview of the tunnel effect of atoms and its physical and chemical properties. The impact of atom tunneling on various fields of chemistry, such as surface chemistry, organic chemistry, biochemistry, and chemistry in the interstellar medium is also discussed.

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