Tunneling Exchange Chemical Reactions in Impurity – Helium Solids

It is common everyday experience that fires can be difficult to start. The reason for this is that most combustion reactions require a threshold temperature or kindling temperature to be reached before they can occur. In starting a wood fire, striking a match can provide the requisite temperature rise. The heat from the burning match helps in two ways. First of all, the reactants undergoing combustion must be brought close enough together to interact. At high temperatures, the components of a flammable substance can move through the material as a result of random thermal motion. The heat from the burning match can facilitate this process. Secondly, for many reactions to proceed, an energy barrier must be surmounted before such reactions can take place, even when the reacting molecules are directly adjacent to one another. The heat from the burning match provides sufficient extra energy to overcome the barrier. This process is called thermal activation and will be completely suppressed at very low temperatures.

Reactions where energy barriers are present can nevertheless occur in certain cases, even when the system under study is at liquid helium temperature, in the range below four degrees above absolute zero. These reactions typically involve very low mass atoms and molecules, and they can be explained only by quantum mechanics. There are two quantum effects that must be taken into account. The first is zero point motion, which is a consequence of the Heisenberg uncertainty principle. Contrary to popular views, all motion does not cease at absolute zero. According to Heisenberg, quantum mechanics requires that some residual motion remain. This zero point motion allows the reagents to diffuse into adjacent positions so that reactions might take place. This process is most effective for reagents with very small masses, which would tend to migrate more readily. The second quantum effect, which is even more spectacular, is the tunneling process that allows reactions to occur even when a large energy barrier is present. Quantum theory tells us that there is a finite probability for a particle to be found on either side of an energy barrier, even when there is insufficient energy to surmount that barrier. A well-known example is the radioactive decay of certain nuclei, which can emit alpha particles (helium nuclei) in spite of the strong binding of the nuclear forces. The concepts of classical physics would never allow this to happen. The escape of the alpha particle from the nucleus certainly defies our intuitions from everyday experience. It is as if we watched a runner pass directly through a hurdle instead of leaping over it. One of the earliest applications of tunneling to chemical reactions involved the polymerization of formaldehyde at very low temperatures.

In the October 21st issue of Physical Review Letters [1], physicists at Cornell working under a NASA grant described studies of spectacular tunneling reactions at liquid helium temperatures in exotic gel-like solids containing solid helium, along with the atomic and molecular forms of the light and heavy isotopes of hydrogen (hydrogen and deuterium). These so-called impurity helium solids form highly porous structures, with liquid helium being contained in the pores. The hydrogen and deuterium atoms and molecules correspond to the impurities in the impurity helium solids. The impurities tend to form small clusters with each impurity cluster being surrounded by thin layers of solid helium an atomic diameter or two in thickness. The structures are bound together by the weak Van der Waals forces.

The Cornell group used electron paramagnetic resonance (electron spin resonance or ESR) techniques applied to hydrogen and deuterium atomic free radicals to help demonstrate the
existence of clusters. (Free radicals correspond to neutral species with unpaired electron spins.) Electrons are known to have intrinsic angular momentum known as spin. Since electrons are charged, the electrons can roughly be considered to be spinning balls of charge. The current associated with rotating charges comprising the electron can generate magnetic fields, just as current through the wire in a coil can generate a magnetic field. Thus the electrons can act like tiny magnets. In ferromagnetic metals all the tiny electronic magnets can work in concert to generate large magnetic fields.

Quantum mechanics tells us that in an external magnetic field the spin axis for the electrons can either be pointing in the direction of the magnetic field or in the opposite direction. Thus only two quantum states are possible. The energies of the two states are quite different. One can think of the analogy of a compass needle which has lowest energy when the north seeking pole points toward the north in the earth’s magnetic field, and the highest energy when the north seeking pole points in a southerly direction. On the microscopic quantum scale, only these two orientations would be possible.

A quantum transition between the two electron states can be induced by applying radio frequency energy with frequency \( f \) given by \( E = hf \) where \( E \) is the energy difference between the two spin states and \( h \) is Planck’s constant. The energy \( E \) depends on the strength of the microscopic electronic magnet and the applied magnet field, in a fashion similar to the above discussion of the compass needle. When the radio frequency of a transmitter is tuned to the correct frequency, the electronic magnets can absorb the electromagnetic waves broadcast by the transmitter. In the ESR technique, a very sensitive detector allows us to determine the correct frequency, which is called the resonant frequency. In addition to the applied external field the electrons can be subject to the influence of other magnetic fields produced by electrons or nuclei in their immediate neighborhood. This may lead to additional sets of resonance frequencies close in value to the resonance frequency in the absence of these effects. In particular, the hydrogen and deuterium atoms each have distinctive ESR spectra due to interactions between the electron magnetic moments and the nuclear magnetic moments. The nuclear moments are a factor of seven larger for protons as compared with deuterons. The nuclear spin angular momentum of the proton is \( h/4\pi \) and that of the deuteron is \( h/2\pi \), where \( h \) is Planck’s constant. As a result of the above, the ESR spectra, called hyperfine spectra, are found to be two widely separated peaks for the hydrogen atoms and three more closely spaced peaks for the deuterium atoms. A graph showing the ESR spectra of hydrogen and deuterium atoms is provided in figure 1. The atomic deuterium and atomic hydrogen spectra show small satellites that are caused by interactions with neighboring \( \text{H}_2 \) or \( \text{HD} \) molecules. This provides evidence that the hydrogen and deuterium atoms are not uniformly distributed throughout the sample but instead concentrated in tiny clusters of \( \text{H}_2, \text{HD}, \text{or} \text{D}_2 \) molecules. Also shown in figure 1 is the forbidden transition of hydrogen atoms as a result of simultaneous spin flips of the electron and proton of a given hydrogen atom. A collaborative effort involving the Cornell group and others at the Brookhaven National Synchrotron Light Source has provided further evidence that clustering occurs. The cluster sizes ranged from 20 to 90 angstroms.

The tunneling exchange reactions studied by the Cornell group are

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\text{D} + \text{H}_2 \longrightarrow \text{HD} + \text{H} \tag{1}
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and

\[
\text{D} + \text{HD} \longrightarrow \text{D}_2 + \text{H} \tag{2}
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FIG. 1. ESR signal from Im-He sample prepared from gaseous mixture H₂:D₂:He = 1:4:100. "H" marks allowed ESR transitions between hyperfine levels of atomic H; "D" indicates hyperfine transitions in atomic D, and "F" indicates the forbidden ESR transition of H atoms. At the bottom are shown typical derivative signals for low field hyperfine lines of (b) hydrogen and (c) deuterium atoms showing both the allowed and the accompanying satellite lines [1].
FIG. 2. ESR spectra for H atoms (doublet) and D atoms (triplet) in H₂-D₂-He solid taken and T = 1.37 K at times: A) $t = 1.38 \times 10^3$ s, B) $t = 1.23 \times 10^4$ s, and C) $t = 2.87 \times 10^4$ s after sample collection. (H₂:D₂:He = 1:8:180)
A group at Chernogolovka, Russia first saw early evidence of the first reaction in impurity-helium solids. Groups in Japan and at the Kurchatov institute observed both reactions in solid hydrogen with very small concentrations of stabilized H and D atoms. The hydrogen and deuterium atoms in the Cornell work were produced by dissociating hydrogen and deuterium molecules in a radio frequency discharge. The resulting mixture of hydrogen and deuterium atoms and molecules was then injected into a beaker containing superfluid helium. The impurity-helium solid containing the hydrogen and deuterium was formed in the beaker, which was then lowered into a resonant cavity where the ESR experiments were performed. The first reaction was too rapid to follow the evolution of the sample as the reaction proceeded, whereas the second reaction proceeded more slowly and could be studied. Since the ESR spectra were different for atomic deuterium and atomic hydrogen, it was possible to monitor the relative amounts of hydrogen and deuterium as time progressed. Figure 2 shows the spectra taken at three different times during the course of these reactions, showing the decrease in the atomic deuterium population and the increase of the atomic hydrogen population. Thus it was possible to observe the kinetics of the second (slower) reaction. The tunneling exchange reactions involving atomic deuterium interacting with molecular hydrogen and hydrogen deuteride can be extremely useful in producing high concentrations of atomic hydrogen in impurity-helium solid samples. It is ordinarily quite difficult to produce samples containing only atomic and molecular hydrogen as the impurities. The reason for this is that such an impurity solid would float and therefore not collect in the superfluid helium in the sample cell. The deuterium tends to weigh the samples down, causing them to sink to the bottom of the beaker. Samples with concentrations as high as \( 7 \times 10^{17} \) hydrogen atoms per cubic centimeter have been obtained.

If the temperature of such samples can be reduced sufficiently, a new set of quantum effects might be observed. The wave-particle duality of quantum theory associates a wave with every material particle. Louis de Broglie first introduced this idea. The wavelength is called the de Broglie wavelength, and it varies inversely as the particle momentum. At low temperatures the particle momenta are expected to be small, and so the de Broglie wavelengths are expected to be long. The system can be described in terms of an average de Broglie wave length or thermal de Broglie wave length \( \lambda \) given by the expression \( \lambda = (2\pi m kT)^{-\frac{1}{2}} \).

As the temperature is lowered, the thermal de Broglie wavelength becomes longer and eventually becomes comparable to the average distance between the hydrogen atoms. At this point the hydrogen ensemble in the sample enters the quantum fluid or quantum solid regime. This could perhaps be associated with the onset of possible exotic effects such as Bose-Einstein condensation of the hydrogen ensemble that could in turn lead to superfluid behavior of the hydrogen atoms. The density of hydrogen atoms is considerably higher in the individual clusters containing atoms and molecules of hydrogen and deuterium. It can be estimated that the density of hydrogen atoms within such a cluster is on the order of \( 10^{20} \) atoms per cm\(^3\), which would correspond to the onset of quantum fluid behavior at \( T \approx 0.35 \) K. This temperature can be reached easily with an ordinary \(^3\)He refrigerator. Another possibility is that of unusual magnetic behavior associated with a magnetic phase transition. The Cornell group is continuing its studies of impurity-helium solids containing large concentrations of hydrogen atoms in hopes of finding these or other exciting effects in this new frontier of research.
References: