



## Chemistry in a Pressure Cooker

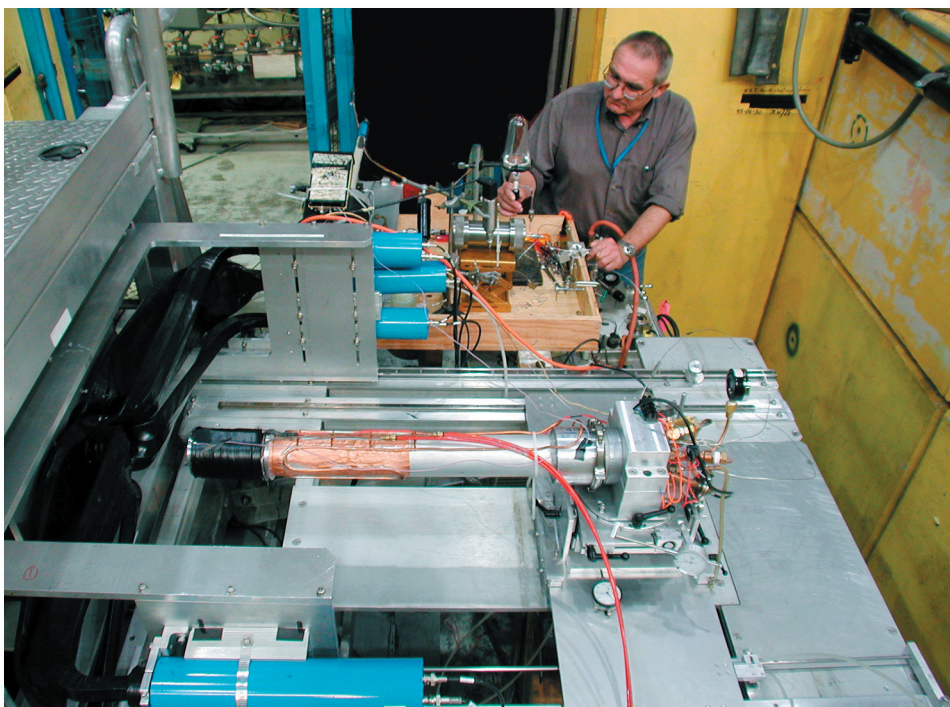
### Free Radical Chemistry under Hydrothermal Conditions

What is the connection between safe destruction of chemical weapons, the development of next-generation nuclear power stations and bacteria which live only near undersea volcanic vents? Answer: they all involve chemistry in superheated water, i.e., in liquid water at temperatures well above its normal boiling point of 100°C. The water remains a liquid because it is under pressure; the combination of high temperature and high pressure is often termed hydrothermal conditions.

These are obviously natural conditions for volcanic vents in the ocean floor, but why choose high temperature and pressure for power generation and waste destruction? In the former case the fundamental consideration is efficiency. A nuclear reactor is a concentrated source of energy, but before this energy can be distributed it must be converted to electricity. This is accomplished by heating water under pressure in the reactor and then allowing it to expand in a steam turbine which drives an electric generator. A fundamental principle of thermodynamics (the 2<sup>nd</sup> Law) states that the maximum efficiency of a heat engine (the turbine) depends on the upper and lower temperatures reached by the working fluid (the water/steam); the greater the difference in temperature, the greater the efficiency. In practice the lower temperature is set by the available cooling – for Ontario power stations this is either Lake Ontario or Lake Huron. Therefore, to improve efficiency engineers look at the high temperature part of the cycle, where pressurised water is heated by flowing through the nuclear reactor. For CANDU reactors the water typically reaches 320°C and 100 atmospheres pressure leading to a theoretical maximum efficiency of less than 50%. It should be stressed that this is the ideal thermodynamic efficiency, and no amount of lubrication or mechanical tinkering

can improve on this. The wasted energy is in the form of chaotic motion (heat), as opposed to the concerted motion capable of doing work. The next generation design of nuclear power stations aims to push the upper temperature to 500 or 600°C. If that is achieved the improved efficiency would generate more electrical power from the same size of reactor.

So why not go ahead and design a pressurised water reactor that operates under these more efficient conditions? Here's where safety and reliability come into consideration. Water at high temperatures and pressures is known to be an extremely corrosive material. What should the pipes be made of, to safely transport the corrosive superheated water around the system? Can corrosion be reduced by adding inhibitors to the water? If so, what happens to these inhibitors when they pass through the high radiation flux of the reactor? It is questions such as these that motivate studies of hydrothermal chemistry. Some initial answers can be found by straight-forward experiments: "Pressure-cook" samples of different



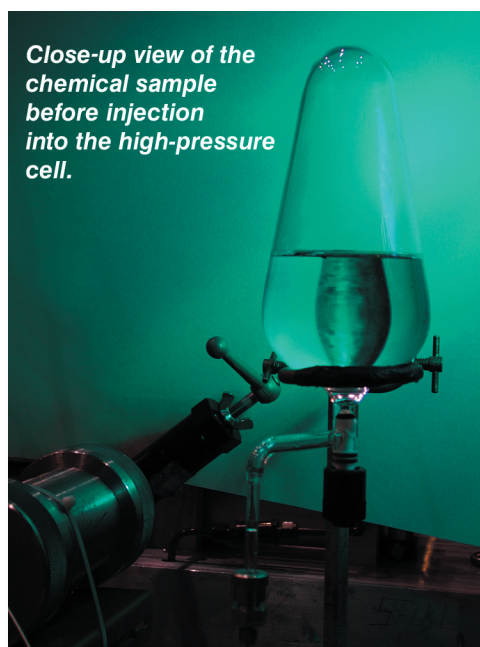
*Dr. Jean-Claude Brodovitch injects a sample of water into the high pressure apparatus, which is the barrel shaped assembly shown in the foreground, temporarily withdrawn from the superconducting magnet and detector assembly (on the left).*

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metals and inspect them for signs of damage. However, trying to predict the behavior of a solution of corrosion inhibitors at different temperatures and pressures, with and without irradiation by ionising particles, requires a very complex model which includes many different physical parameters whose values are mostly unknown. The situation is particularly complicated for problems concerning potential radiation damage, since the relevant reactions involve highly reactive free radicals. Ideally one wants to study these processes in real-time; in practice this is next to impossible.

Safety and efficiency are also paramount when one considers methods to destroy hazardous waste. Volatile organic compounds from laboratories and homes (cleaning fluids, paint thinners, etc.) are usually incinerated, but what about more hazardous material? The Chemical Weapons Convention requires the U.S. to destroy over 30,000 tons of chemical weapons by April 2007. However, the residents of Tooele, Utah became a little nervous when they found out that the U.S. Army was burning sarin (6,000 tons) and VX nerve gas (7,600 tons) in their neighborhood. The problem with incineration is that you start with a controlled quantity of flammable liquid, mix it with air, expose it to a flame, and hope that by the time the very large volume of gaseous products reaches the smoke stack there is nothing nasty left over. In Canada, PCBs and ozone-depleting chemicals are burnt at the Swan Hills facility in Alberta. The license requires 99.9999% destruction. From time-to-time the facility has been shut down because environmental monitoring showed that toxic by-products (e.g. dioxins and furans) had been released. Scientists, who understand risk and realise that 100% efficiency is never attainable, are less concerned about such events than the general public. Chemists routinely handle bucketfuls of



*Close-up view of the chemical sample before injection into the high-pressure cell.*

such “deadly” chemicals without any consequences to themselves or others. On the other hand, because of the much higher risk, disposal of tons of nerve agents has to be dealt with in better ways.

An alternative to incineration is supercritical water oxidation (SCWO). From the chemical point of view the toxic organic material is still burned (oxidised), but it is done under water! This is possible because of the remarkable change in properties of water as it is heated to its so-called supercritical state. Under normal conditions water dissolves ionic materials (salts) but it does not mix with non-polar organics (oils). However, supercritical water is much less polar and behaves more like an organic solvent. This means it readily dissolves chemical warfare agents and other toxic materials, which can then be destroyed by the addition of oxygen or other oxidising material. The main products are the same as for incineration in air: carbon dioxide and water. However, in water the toxic elements (chlorine in PCBs, sulphur in mustard gas, phosphorus in nerve agents) are precipitated in harmless form as inorganic salts.

The idea of burning material under water seems contradictory but it has been shown to work. It is even possible to sustain a flame in water at high temperatures and pressures (typically 600°C and 300 atmospheres pressure). This can be done by piping oxygen into hot water containing a hydrocarbon such as methane. The flame is similar to a regular natural gas flame burning in air, except that in supercritical water the oxygen is inside the flame and the combustant is in the “atmosphere” around it.

The most important aspect of SCWO technology is that the oxidation process occurs in a sealed vessel – a giant pressure cooker – so the hazardous material remains contained until after tests confirm its destruction. The necessary engineering technology has been developed over the past decade, and SCWO





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is being implemented in a full-scale pilot plant facility at the Blue Grass Army Depot in Kentucky.

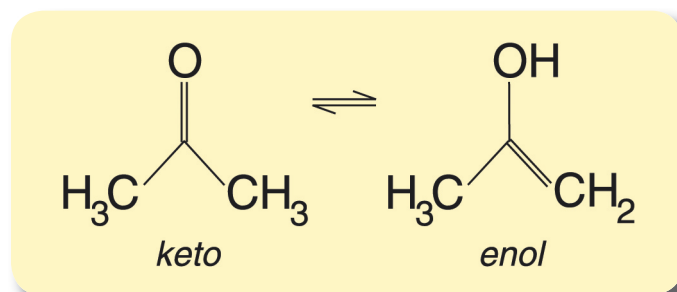
However, the chemical details are far from clear. It is possible to find the best operating conditions to destroy a specific agent by trial and error, but to predict what happens to a wide variety of hazardous materials requires detailed chemical knowledge and modelling. Like the radiolysis problem mentioned earlier, combustion involves free radical intermediates whose properties and behavior under hydrothermal conditions are mostly unknown.

This is the motivation for carrying out detailed chemical studies of hydrothermal systems, but how to do it is no simple matter! Most studies to date have relied on end-product analysis and modelling to infer multi-step reaction sequences. Much better would be direct measurement of reaction intermediates in real-time in situ. The modern chemist has a variety of spectroscopic tools that are usually applied to such problems; tools that permit the identification and monitoring of different chemical species according to their specific molecular properties, such as the vibration frequency of particular chemical bonds. The problem is that the application of these conventional techniques is often limited by the technical demands of the harsh environment. For example, how do you get light in and out of a pressure cooker? Even special optical windows made of sapphire or diamond are corroded by supercritical water.

TRIUMF has particular expertise at probing chemistry in extreme environments by using  $\mu$ SR, a magnetic resonance technique that uses the muon as a spin probe. Since a positive muon can act as the nucleus of a hydrogen-like atom, muonium (Mu), it can be used to study H atom reactions and free radicals incorporating H. High-energy muons can be created to penetrate into a pressure vessel and thermalise in the material of interest. The window of a pressure cell is made of titanium and is over 2 mm thick. Muons have a mean lifetime of only 2.2 microseconds, but when they decay they emit positrons, most of which have enough energy to pass through the walls of the pressure cell and thus carry information to the outside. The apparatus is placed in a large electromagnet so that the muon spins precess

with frequencies characteristic of their chemical environment. In this respect the technique is similar to the well-known magnetic resonance imaging (MRI) used in medicine.

Muons are particularly effective at “spying” on free radicals, for which other techniques are less effective. Consider, for example, what happens when a hydrogen atom reacts with acetone in water. Under normal conditions the acetone exists in the keto form, with a minuscule amount in the enol form. At higher temperatures it is expected that the equilibrium shifts towards the enol:

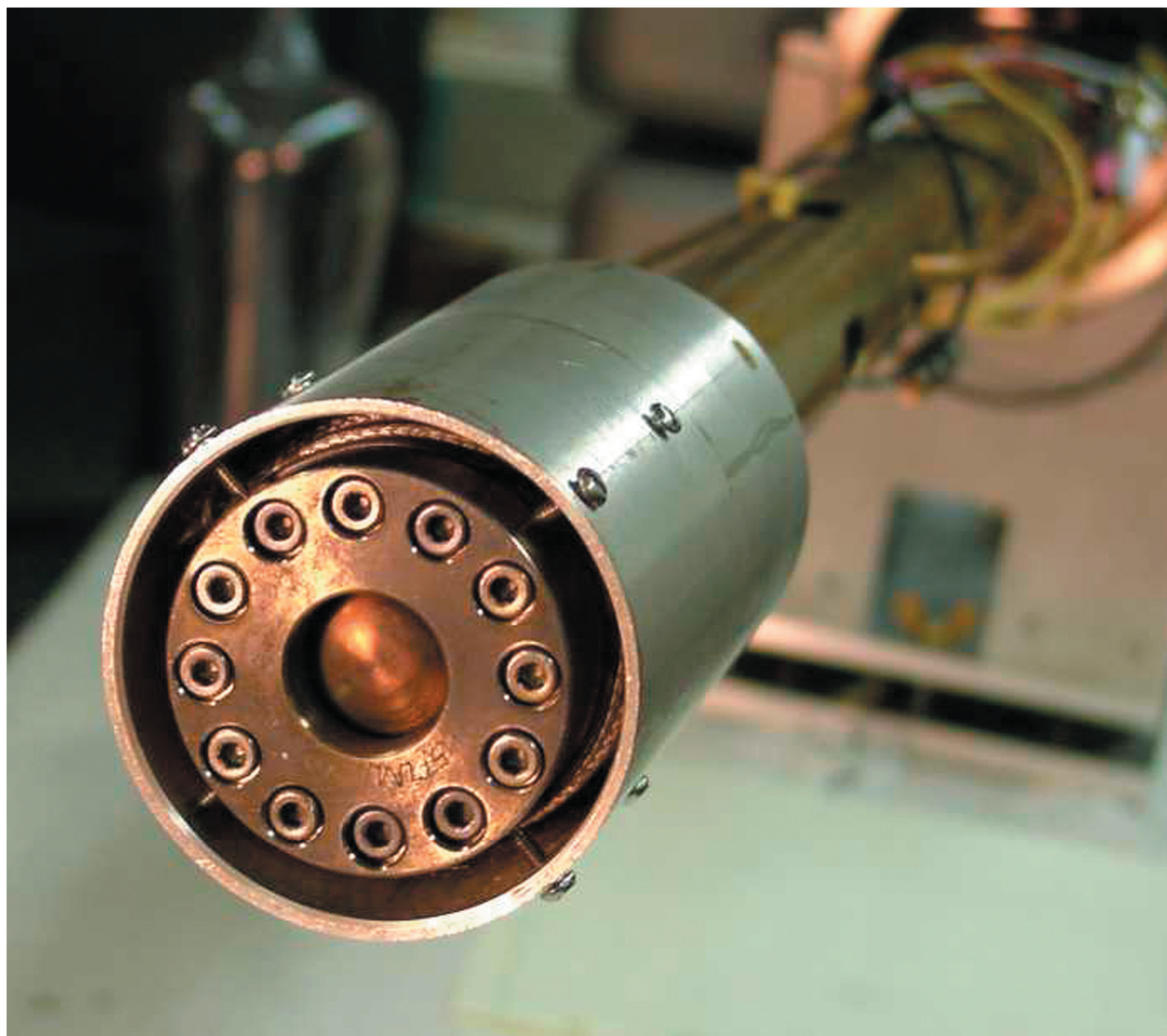


The reaction of a hydrogen atom with the enol form is much faster than for the keto form, but ironically, the same free radical product is formed. By studying the two reactions with muonium it is possible to tell them apart – reaction with the keto form gives the radical with Mu attached to the oxygen atom, whereas reaction with the enol results in incorporation of Mu in a methyl ( $\text{CH}_3$ ) group. Experiments at TRIUMF have clearly shown that the keto route is dominant at low temperatures but that above 250°C the enol adduct is formed. This was a completely novel result; literature data on the keto enol equilibrium by conventional means is limited to 55°C!

The practical problems of studying complex chemistry in a SCWO waste destruction facility are similar to those facing the designers of CANDU-X, the next generation of Canadian nuclear reactors. Kinetic data on radiolysis transients (H atoms, hydroxyl radicals, hydrated electrons, etc.) is so difficult to obtain that the current generation of pressurised water reactors is based on AECL models of water chemistry that rely on extrapolation of lower temperature measurements. TRIUMF measurements

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*Muon's-eye view of the target cell, which is made of titanium and can withstand pressures of 500 atmospheres at temperatures up to 500 °C. The dome shaped window (in the middle) is over 2 mm thick.*

on muonium kinetics have shown that the AECL extrapolations fail at high temperature, where there is a transition from liquid-like to gas-like behavior. At one time AECL was a world leader in high temperature water radiolysis, but personnel have since been directed to other projects. As a consequence, reactions of H atoms and other radiolysis transients have only been studied at temperatures up to about 200°C, far below the 500 to 600°C being considered for CANDU-X, and even below the limit (450°C) reached in muonium kinetics studies.

The muonium chemistry research mentioned in this article was carried out by a team from the

Chemistry Department of Simon Fraser University supported by the TRIUMF Centre for Molecular and Materials Research. The existence of the latter support group is an essential prerequisite in bringing to TRIUMF experts in the particular scientific problems under study. The success of the UBC and SFU muonium chemistry groups has demonstrated that TRIUMF is much more than a facility for nuclear and particle physics.

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