

## CHAPTER 1

# EXPLORING CHEMISTRY IN EXTREME ENVIRONMENTS: A DRIVING FORCE FOR INNOVATION

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### 1. Introduction

Our understanding of chemical dynamics has become increasingly more detailed as experimental and theoretical methods have advanced. One of the ultimate goals of these endeavors is to develop reliable, predictive models so that we can foretell the detailed outcome of chemical reactions. The motivation to develop such predictive capabilities is often driven by the need or desire to understand and describe the chemistry in some extreme environments. These extreme environments, with conditions well outside the range of common room temperatures or pressures, can be natural or manmade,

and can be part of our everyday experience or far from our terrestrial domain. In many cases, reproducing these extreme environments push experimental and theoretical methods beyond their current limits, necessitating innovation and new developments to describe the chemical dynamics in these regimes. In all cases, a close interplay between experiment and theory is required to develop and validate our descriptions.

In this overview, I will look at a range of examples of extreme environments, and discuss the innovations that are being spawned to address experimental and theoretical challenges. Comprehensive reviews of many of these areas already exist in the literature and are not the intent of this chapter. Nor will I focus on work discussed extensively elsewhere in this volume. Instead, selected examples of current research will be discussed in which innovation in dealing with extreme environments has led to some insights in our understanding of chemical dynamics.

Table 1 lists a variety of environments that can be considered extreme and are the subject of chemical studies. It is difficult to develop general quantitative criteria as to what constitutes an extreme environment. Such categorizations must be viewed from the perspective of the type of system under consideration. For a liquid lubricant in an engine, a temperature of 620 K, above its decomposition temperature, is an extreme environment. For metals exposed to high temperatures, such as titanium and nickel superalloys in aerospace vehicles, temperatures of 1100 and 1400 K, respectively, test their operational limits. In these two cases, thermal degradation of the

**Table 1.** Conditions in some extreme environments.

Environment	Temperature (K)	Pressure (Pa)
Superfluid helium	< 2.7	
Solid hydrogen	< 4.0	
Earth's atmosphere (100–400 km)	200–2000	
Hydrothermal vents	600	$2\text{--}3 \times 10^7$
Aircraft engine lubricants	620	
Aircraft engine components	2300	$1 \times 10^7$
Rocket nozzles	2000–4000	$1\text{--}2.5 \times 10^7$
Burning meteoroid	4000	
Detonation of solid explosive	3000–4000	$2\text{--}4 \times 10^{10}$
Earth's core	4000	$4 \times 10^{11}$

Note:  $10^5$  Pa = 1 bar  $\cong$  1 atm; 1 GPa = 10 kbar  $\cong$   $10^4$  atm.

material via bond breakage or chemical reactions such as oxidation can alter the properties of the materials and set the limits for their working environments.

There are a number of natural environments under extreme conditions that have attracted considerable chemical attention. The geochemistry of the earth's interior occurs at temperatures of up to 4000 K and pressures up to 400 GPa.<sup>1,2</sup> In hydrothermal vents on the ocean floor where unique life forms are cultivated, chemistry occurs at temperatures of 600 K and pressures of 20 to 30 MPa.<sup>3,4</sup> The earth's atmosphere also provides a collection of extreme environments. Studies of chemistry in the stratosphere and in polar stratospheric clouds have motivated a wide range of studies at low temperatures and have contributed to our understanding of homogeneous and heterogeneous chemical reactions.<sup>5,6</sup> Meteoroids burning in the atmosphere produce temperatures of 4000 K, and generate a unique high temperature chemistry of metals and metal oxides. (See Chap. 6 of this volume by Dressler and Murad). Charged particles in the upper atmosphere are accelerated by the earth's magnetic field near the poles leading to high energy collisions that produce aurora and interesting chemistry.<sup>7</sup> Considerable attention has also been devoted to the chemistry of other planets and their atmospheres,<sup>8</sup> and the chemistry of their satellites.<sup>9</sup> (Also, see Chap. 8 in this volume by Johnson).

A wide range of manmade circumstances and technological applications also create an important set of extreme environments. Cutting-edge technological applications often stress materials to their limits. For example, combustion processes in rocket engines can occur at temperatures up to 4000 K, and pressures of 25 MPa.<sup>10</sup> In some aircraft engines, efficiency is sacrificed to prevent material failure due to excessive temperatures. Metal parts in aircraft engines are often protected by thermal barrier coatings made of ceramics in order to extend their operating temperature range. (See Chap. 10 in this volume by Christensen, Ashe and Carter). The high temperature stability of the materials on the outer skin of aerospace vehicles also limit performance. The outer skin of a transatmospheric aerospace vehicle would be expected to reach temperatures on the order of 1100 K from the frictional heating of the skin by gas-surface collisions with molecules in the atmosphere.<sup>11</sup> Leading edges of wing surfaces and the walls of the engine inlets could reach temperatures of 1700 K and 2000 K, respectively.<sup>11</sup>

Chemistry at high pressures also has many technological applications. Chemistry in supercritical fluids, for example, is drawing increasing attention for the possibility of replacing organic solvents in synthetic, purification, and separation processes.<sup>12</sup> Extremely high pressure (20–40 GPa)<sup>13</sup> and temperature (3000–4000 K)<sup>14</sup> transients are experienced in the detonation of energetic materials. The study of the chemistry in the detonation front of explosives is an area where experimental research<sup>15</sup> and novel computer simulations (see Chap. 11 of this volume by White) are underway to understand the real time effects on energy transfer and chemical processes. On a microscopic scale, extremely high local pressures can be created at the interface where two materials slide across one another. The pressures produced at the junction where asperities come in contact can reach 1 GPa, exceeding the critical stresses beyond which the materials deform or fracture.<sup>16</sup> A satisfactory understanding and picture of all of these processes will likely rely on the development of reliable simulation methods, developed and validated in close collaboration with experiment.

Another classification of environments that can be considered extreme are highly chemically reactive environments. The sparse but reactive environment of space, the technologically important realm of plasma processing, and chemical laser systems fit into this category. A number of these situations are discussed by Minton (see Chap. 9 in this volume) who looks at the reactions of oxygen atoms with the low-earth orbital translational energy of 5 eV as they collide with spacecraft materials, and Heaven (see Chap. 4 of this volume) who discusses dynamics in chemical laser systems. Again, experiment and theory together must provide a well-grounded, fundamental understanding of the dynamics of these systems if a reliable predictive capability of the macroscopic observables is to be developed.

## **2. Chemistry at High Temperatures and Pressures**

The drive to model the chemistry in flames, in other combustion systems, and in high enthalpy air flows has motivated many studies of chemistry at high temperatures and pressures. Many studies of elementary processes under these conditions have been performed in shock tubes, typically at temperatures in the range 1000 to 2000 K, but temperatures up to 5000 K can be achieved in these devices. In a typical shock tube experiment, a driver gas is stored at high pressure behind a diaphragm, separating it from the sample residing in the length of the tube. When the diaphragm

is ruptured, a shock wave travels down the tube, and measurements are often made near the end wall of the tube behind the reflected shock where relatively constant, elevated temperatures can be maintained for hundreds of microseconds. Shock tube work has been reviewed periodically and extensively.<sup>17-19</sup> In fact, much of the existing high temperature rate data frequently used in models of combustion chemistry and other high temperature gas-phase systems has been obtained in shock tubes.<sup>20</sup>

Alternative approaches to measuring reaction rates and dynamical processes at high temperatures have been pursued. Measurements in flames using laser diagnostics<sup>21</sup> and molecular beam mass-spectrometric sampling have been carried out.<sup>22</sup> Direct laser heating of molecules in the gas-phase or heating of an absorbing gas to create a heated channel of gas far from surfaces have been used to obtain mechanistic information and quantitative Arrhenius parameters for homogeneous reactions in the gas-phase.<sup>23,24</sup> The high heating and cooling rates obtained by pulsed-laser-driven heating can produce temperatures in excess of 1000 K that last for only several microseconds. Thus, products of the initial high temperature reaction are often rapidly cooled and thermally stabilized relative to experiments at constant high temperatures. This permits analysis of primary dissociation products that can themselves often thermally dissociate.<sup>25</sup>

Novel methods are now being developed to generate shock waves that rapidly produce extreme environments of high pressure and temperatures in solid materials. Shock wave generation, propagation, and their effects on the chemistry of the material are particularly important in energetic materials, where a shock wave, initiated by a physical impact, could lead to detonation. Studies have been performed in which gas guns are used to propel a large impact plate into a sample, generating pressures of up to 200 GPa. The shocked sample can then be spectroscopically probed in single shot experiments,<sup>14,26</sup> with these spectroscopic studies usually performed in the tens of GPa pressure region. But ultrafast time resolution and precise control of the timing between shock and probe is required to unravel the initial physical and chemical changes and vibrational energy redistribution in condensed-phase materials and to study their evolution following passage of a shock front. New methods have recently been developed to probe these properties in real time, and are providing new insights into the behavior of these materials that directly impact their chemical reactivity.<sup>15</sup>

Clott and coworkers<sup>27,28</sup> have developed a technique to generate shock waves with fast ( $< 25$  ps) risetimes in specially designed assemblies, that are

then probed spectroscopically. In this method, a near-infrared laser pulse is absorbed by a 2- $\mu\text{m}$  thick outer layer of a microfabricated, multilayered target array. A few nanograms of this polymer layer are rapidly ablated and a shock wave that is relatively planar, and of approximately constant velocity throughout the sample is launched into the layers below. A buffer layer delays the arrival of the shock at the sample layer as debris from the ablation is permitted to clear. The shock then impinges on the sample layer, and subsequently travels into a dissipation layer. This layered assembly is supported on a glass substrate which provides optical access for probing by coherent anti-Stokes Raman spectroscopy. This “nanoshock” method has produced transient pressures on the order of 1–5 GPa and temperature rises of several hundreds of degrees in a region about 100  $\mu\text{m}$  in diameter. Since the sample is locally destroyed by the ablation of the shock-generation layer, the sample assembly is translated before the next shot is fired, and reproducible shocks have been generated at a repetition rate of 80  $\text{s}^{-1}$ .

The “nanoshock” method allows the collection of vibrational spectra of molecular solids with time resolution of 25 ps. It has been applied to a number of energetic materials.<sup>29</sup> The rapid cooling during unloading of the shock ( $\sim 10^{11}$   $\text{K s}^{-1}$ ) allows little time for thermal decomposition of the sample. This method has recently been used to detect fast mechanical processes in polycrystalline films of the energetic material NTO.<sup>30</sup> The shocks induce partial orientation of the crystals with one another in only a few nanoseconds. This orientation is faster than the time scale for initiating chemical reactions in this system, and may have implications for the mechanism of the initiation of detonation of energetic materials. The importance of orientation in detonation has been previously observed in the directional dependence of shock-wave initiated detonation of single crystals of energetic materials.<sup>31</sup>

The detonation of energetic materials is also critically dependent on energy transfer in molecular solids.<sup>32</sup> Studies of vibrational energy redistribution in polyatomic molecules in the condensed-phase are being carried out on a number of systems.<sup>33,34</sup> Resonant vibrational excitation from ultra-short infrared pulses can drive molecules to effective vibrational temperatures of 4000–5000 K. Vibrational energy redistribution can then be studied by anti-Stokes Raman probing. These IR–Raman studies, with time resolution of about 1 ps, monitor the energy flow throughout almost all of the vibrational states of a polyatomic liquid. A particularly relevant case for

energetic materials is nitromethane, a model system for detonation. When the C–H stretching modes of nitromethane are excited, vibrational cooling is observed to occur in three distinctive steps.<sup>34</sup> First, the deposited energy is redistributed to all of the vibrations of the molecule in a few picoseconds. Second, the higher frequency vibrations relax to lower energy modes in a few tens of picoseconds. Finally, these lower energy modes decay to the bath in about 100 ps. The dynamics of coupling of energy into these lowest frequency modes may play a key role in determining the sensitivity of an energetic material to shock initiation.

Other novel methods are being employed to examine chemistry at extremely high temperatures and pressures. For example, Suslick and co-workers use ultrasound to initiate “sonochemistry.”<sup>35,36</sup> In this work, ultrasound is directed into a liquid creating bubbles that grow, and then implisively collapse. The rapid collapse, or cavitation, compresses and heats the gas trapped in the bubble producing hot spots with effective temperatures of  $\sim 5000$  K, pressures of  $\sim 100$  MPa, and heating and cooling rates above  $10^{10}$  K s<sup>-1</sup>. Sonoluminescence, the light that is often produced during cavitation, can provide a probe of the interior of the bubble. The intense temperatures and pressures produced during cavitation can have destructive effects, for example, when it occurs around the propeller of a ship. However, these conditions have been used for some novel chemical synthesis, with particular effect when solid surfaces or powders are in the liquid.<sup>37</sup> In these systems, solid particles are accelerated to high velocities and interparticle collisions can change surface morphology and chemical reactivity. Unique nanostructured materials and biomaterials have been synthesized by these methods.<sup>38,39</sup>

Studies at extremely high static pressure can be carried out in diamond anvil cells.<sup>40</sup> Studies of chemical dynamics in gem anvil cells are beginning to be carried out,<sup>41</sup> and some unique chemical synthesis can also occur at these high pressures. For example, a high pressure polymerized phase of carbon monoxide was recently reported to be synthesized using visible laser light to irradiate a carbon monoxide sample at pressures of over 5 GPa in a diamond anvil cell.<sup>42</sup>

Another class of extreme environments being used for synthetic applications are near critical and supercritical fluids. A number of reviews have looked at reactions in supercritical water.<sup>43,44</sup> Brill and coworkers have developed experimental devices in which to perform infrared and Raman

spectroscopic studies of hydrothermal reactions at temperatures up to 700 K and pressures of 35 MPa,<sup>45,46</sup> above the critical point of water (647 K, 22.1 MPa).<sup>47</sup> These studies have elucidated the kinetics and reaction pathways of numerous systems under hydrothermal conditions.

Studies of solvation and energy transfer in supercritical fluids provide an important way to bridge our understanding of dynamics in the gas-phase and liquid phase.<sup>48</sup> Troe and coworkers have performed studies in supercritical fluids to test the applicability of the Isolated Binary Collision (IBC) model of energy transfer over a wide range of density and temperature, spanning the transition from gas-phase to liquid phase.<sup>49,50</sup> In these experiments, subpicosecond lasers were used to excite azulene with about  $20\,000\text{ cm}^{-1}$  of energy to its first excited singlet state,  $S_1$ . This state rapidly underwent internal conversion producing highly vibrationally excited levels of the ground electronic state,  $S_0^*$ . Deactivation of the vibrationally excited azulene by collision partners (Xe,  $\text{CO}_2$ , ethane, propane, *n*-pentane, *n*-octane) was monitored by transient absorption in the ultraviolet on the  $S_3 \leftarrow S_0$  transition. These experiments, coupled with Monte Carlo simulations, demonstrated that an IBC model of energy transfer proved applicable from densities that spanned the gas-phase to the liquid phase if the collision frequency was expressed in terms of the radial distribution function around the azulene solute molecule, assumed to be a hard sphere in a Lennard-Jones fluid.<sup>50</sup> The radial distribution function accounts for the local cluster formation or solvation that dynamically occurs in supercritical fluids. This clustering increases the local density of the solvent around the solute with respect to the bulk and could be thought of as shielding the excited molecule. This model implies that while the collision frequency varies with density, the average energy transferred per collision  $\langle \Delta E \rangle$  remains constant as a function of density, and should be transferable from gases to liquids.<sup>50</sup>

Another probe of the local environment around the azulene solute molecule was the shift of the frequency of the  $S_3 \leftarrow S_0$  absorption band, as a function of density.<sup>50</sup> This solvachromic shift, or stabilization of the electronic states of the solute in the presence of the solvent, was accurately described using the same radial distribution function used to reproduce the collisional deactivation rates. The applicability of the same radial distribution function to treat collisional deactivation and solvachromic frequency shifts suggests that both have a similar dependence on local density.

Fayer and coworkers have studied the vibrational dynamics of molecules excited in solvents that were in or near supercritical conditions.<sup>51-54</sup> They

have observed very interesting behavior in the vibrational lifetime,  $T_1$ , as a function of density and temperature near the critical points. In these experiments, a CO stretching vibration in  $W(\text{CO})_6$  was excited to  $v = 1$ , and its lifetime was measured using picosecond infrared lasers. In supercritical  $\text{CO}_2$ , just above the critical temperature, the vibrational lifetime decreased from over 900 ps to about 700 ps as the density increased from about 2 to 5 mol  $\text{L}^{-1}$ . The lifetime then reached a plateau, and remained constant in the density range 7 to 12 mol  $\text{L}^{-1}$ , before beginning to decrease again at higher densities.<sup>51,52</sup> At constant, near-critical density, vibrational lifetimes were studied as a function of temperature.<sup>53,54</sup> Temperature regimes were found in supercritical ethane and fluoroform where the vibrational lifetime increases with increasing temperature. In supercritical  $\text{CO}_2$ , however, the lifetime decreased approximately linearly with temperature. These interesting and carefully collected data are providing some nonintuitive results that are challenging tests for theories to describe the intermolecular interactions near the critical point.

### 3. High Temperature Chemistry in the Atmosphere

The earth's upper atmosphere possesses a collection of extreme environments. For example, at altitudes between 100 and 400 km, the temperature of the atmosphere rises from 200 K to 2000 K. In this region of the ionosphere, the dominant ions are  $\text{O}_2^+$ ,  $\text{NO}^+$ , and  $\text{O}^+$ , having concentrations between  $10^4$  and  $10^5$   $\text{cm}^{-3}$ .<sup>55</sup> Until recently, it has not been possible to measure reaction rates for these species throughout the range of temperatures characteristic of the ionosphere. The need to validate rate constants for use in computational models of the ionosphere has spurred the development of instruments to obtain this data.

Viggiano, Morris, and coworkers have developed a high temperature flowing afterglow that they have used for studying ion-molecule reactions at temperatures from 300 K to 1800 K.<sup>56</sup> The high temperature capability enables the observation of the onset of higher energy reaction channels, and combined with data from previous studies, provides insights into the role of internal energy in promoting reactivity. Examples of this are the reactions of  $\text{O}^+$  with  $\text{N}_2$  and  $\text{O}_2$ ,<sup>57</sup> where prior work in drift tubes had been used to selectively enhance translational energy.<sup>58</sup> Comparing the rate constants obtained using pure thermal excitation with those from nonthermal, translational excitation, it was determined that rotational energy plays a

minimal role in controlling reactivity, while vibrational excitation has a much greater, enhancing effect.<sup>57</sup> In the case of the reaction of  $O^+$  with  $O_2$ , thermally exciting vibrations increased the reaction rate constant a factor of 5 over the same energy obtained by pure translational excitation. For  $O^+$  with  $N_2$ , it was found that thermally exciting  $N_2$  to  $v = 2$  increased the reaction rate constant by a factor of 40 relative to the  $N_2(v = 0)$  rate constant, in agreement with earlier observations of Schmeltekopf *et al.*<sup>59,60</sup> The role of vibrational excitation in enhancing reactivity has recently also been observed in the reactions of  $N^+$  and  $N_2^+$  with  $O_2$ <sup>61</sup> and in the reactions of  $O^+$  with  $CH_4$ ,<sup>62</sup> where new product channels were seen to open as  $CH_4$  became vibrationally excited due to high thermal excitation. Wodtke and coworkers<sup>63</sup> have also recently reported that vibrational excitation can promote surface chemistry. They observed that NO molecules excited to  $v = 13$  and 15 react (via dissociative adsorption) with a copper surface with a reaction probability more than one thousand times greater than for ground state NO.

Ion beam experiments involving high temperature vapors are also being carried out. Levandier *et al.*<sup>64</sup> have developed a high temperature guided-ion beam apparatus in which reaction cross sections can be measured at selected translational energies and target vapor temperatures up to 800 K. While the instrument was originally designed for metal vapor studies, it has also been used to investigate the change in threshold behavior when low-frequency modes of a molecular target are thermally excited.<sup>65</sup> Studies in this system related to meteor chemistry are discussed in more detail in Chap. 6 by Dressler and Murad in this volume.

Another example of a chemically interesting property of the upper atmosphere is nonlocal thermodynamic equilibrium (NLTE). Rotational NLTE has been demonstrated by the observation of pure rotational emission<sup>66–68</sup> from high N levels of OH, NO, and CO in the upper mesosphere/lower thermosphere (85 to 95 km) where pressures are about 5 Pa. For OH ( $X^2\Pi$ ,  $v = 0–3$ ), emission from rotational levels up to  $N = 33$  were observed in the airglow in the CIRRIS 1A experiment conducted on the space shuttle.<sup>66</sup> Holtzclaw *et al.*<sup>69</sup> have studied the rotational relaxation of high N states of OH ( $X^2\Pi$ ,  $v = 1–3$ ) by  $O_2$  in a cryogenically-cooled chamber called LABCEDE at 100 K to assess the processes that affect the rotational distribution of OH in the upper atmosphere. They found that rotational relaxation occurred at a gas-kinetic rate, predominantly by single-quantum steps within each vibrational manifold.

## 4. Low Temperature Chemistry

Moving from the earth's upper atmosphere to the outer planets and interstellar space,<sup>70</sup> lower temperature environments become more important. Recent reviews of ion–molecule reaction dynamics<sup>71</sup> and gas-phase reactivity and energy transfer between neutral species at very low temperatures<sup>72</sup> (below 80 K) describe the current status of these fields. An interesting approach developed by Rowe and coworkers is the CRESU (Cinétique de Réactions en Ecoulement Supersonique Uniforme) technique that has been applied to both ion–molecule<sup>73,74</sup> and neutral–neutral chemistry.<sup>75–78</sup> In this method, reaction kinetics are studied in the expansions of Laval nozzles. These isentropic expansions produce gas flows that are relatively high in density ( $10^{16}$ – $10^{17}$  molecules  $\text{cm}^{-3}$ ) and have enough collisions to maintain thermal equilibrium. The uniform temperature, density, and pressure of this method makes it well suited for kinetic measurements down to temperatures around 10 K. In studies of neutral–neutral reactions in the CRESU apparatus, laser photolysis production of radicals or other transient species is coupled with laser-induced fluorescence detection. Van Marter and Heaven<sup>79</sup> have also recently used Laval nozzles to study energy transfer between iodine atoms and  $\text{O}_2$  ( $a^1\Delta$ ) at temperatures down to 150 K. This regime is of importance to the chemical oxygen iodine laser when operated in a supersonic expansion (see Chap. 4 by Heaven in this volume).

As is often the case, experiments outside the range of previous measurements have provided unexpected results, highlighting the need for caution when extrapolating results beyond the temperature range in which they were obtained. The low temperature studies in the CRESU apparatus have shown that a large number of reactions have rates that increase as the temperature is decreased.<sup>72</sup> This behavior seems characteristic of reactions with no barrier, and are dominated by long-range attractive forces between reacting species that lead to capture. The intermediate complex formed can allow reagents time to find the appropriate orientation for reaction to take place, as has been argued<sup>76</sup> for  $\text{CN} + \text{C}_2\text{H}_6$ , or can mediate a series of H atom transfers as in the reaction of  $\text{CN} + \text{NH}_3$ .<sup>75</sup>

Due to the inverse temperature dependence of the Arrhenius relationship, these very low temperature studies cover a wide range on an Arrhenius plot. Combining CRESU results with higher temperature studies enables the competition of reaction channels with opposing temperature dependencies to be observed in some reactions. This produces an Arrhenius plot

that has a minimum at intermediate temperatures, while the rate constant increases with increasing temperature at high temperatures and increases with decreasing temperature at lower temperatures. Such behavior has been argued to imply for the  $\text{CN} + \text{C}_2\text{H}_6$  reaction that a tight transition state dominates at high temperatures, while a loose transition state controls the reaction at low temperatures.<sup>76</sup> This transition between different dynamics in different temperature regimes has previously been observed in some ion–molecule reactions<sup>71,80,81</sup> and radical–molecule reactions that have been studied over wide temperature ranges.<sup>82–85</sup>

Troe and coworkers have been able to study chemical processes over a very wide range of pressures as well as a wide temperature range. For example, they have studied the recombination reaction of  $\text{O} + \text{O}_2$  to form  $\text{O}_3$  at temperatures down to 90 K and pressures up to 100 MPa.<sup>86</sup> Their studies of reactivity and energy transfer have been instrumental in developing a unified understanding of reactivity and energy transfer over an extremely wide range of conditions, including the transition from the gas-phase into the condensed phase.

At even lower temperatures, some unusual properties of matter are displayed. Consequently, new experimental and theoretical methods are being created to explore and describe chemistry in these regimes. In order to account for zero-point energy effects and tunneling in simulations, Voth and coworkers developed a quantum molecular dynamics method that they applied to dynamics in solid hydrogen.<sup>87,88</sup> In liquid helium, superfluidity is displayed in  $^4\text{He}$  below its lambda point phase transition at 2.17 K. In the superfluid state, helium's thermal conductivity dramatically increases to 1000 times that of copper, and its bulk viscosity drops effectively to zero. Apkarian and coworkers have recently demonstrated the disappearance of viscosity in superfluid helium on a molecular scale by monitoring the damped oscillations of a 10 Å bubble as a function of temperature.<sup>89</sup> These unique properties make superfluid helium an interesting host for chemical dynamics.

The ability to dope impurity atoms or molecules into large helium clusters by a pick-up method, pioneered by the groups of Toennies<sup>90</sup> and Scoles,<sup>91</sup> has helped make studies in superfluid helium clusters more accessible. In this method, an expansion through a nozzle produces a beam of helium clusters. Under appropriate conditions, helium droplets comprising up to  $10^6$  helium atoms can be formed. These droplets then traverse a collision cell containing a foreign gas at a pressure of  $10^{-4}$ – $10^{-3}$  Pa. Atoms or

molecules in the collision cell become embedded in the droplet, typically evaporating several hundred helium atoms from the droplet for each dopant species picked up. The beam of helium droplets doped with a guest species emerging from the collision cell can then be studied by a number of diagnostic methods.

The spectroscopy of doped helium clusters has recently been reviewed from an experimental<sup>92</sup> and theoretical perspective.<sup>93</sup> The inviscid nature of the helium clusters was demonstrated by Toennies and coworkers who, using rovibrational spectroscopy, demonstrated that SF<sub>6</sub> and OCS were nearly free rotors in <sup>4</sup>He clusters.<sup>94,95</sup> Nauta and Miller have utilized the vanishing viscosity and superthermal conductivity of superfluid helium to create unprecedented molecular assemblies among dopants in helium clusters.<sup>96</sup> In that work, nine HCN molecules were successively picked up by a helium cluster and then self-assembled into a straight-line chain controlled by the long-range dipole–dipole forces among them. The high thermal conductivity of the bath effectively couples energy away before the molecule can rearrange to a lower-energy minimum on the potential energy surface. The potential ramifications to chemical dynamics of such a fast energy-dissipation process competing with intramolecular energy redistribution are intriguing.

## 5. Conclusions

The need to understand and model chemistry in extreme environments has long been a driving force for innovation in experimental and theoretical chemistry. As has been shown, a wide range of novel methods and systems have been developed to explore chemistry in these regimes. The conditions that can be achieved in some of these laboratory systems are listed in

**Table 2.** Experimental methods that produce extreme environments.

Experimental method	Temperature (K)	Pressure (Pa)
Helium droplets	< 2.7	
Laval nozzles/CRESU	10–200	
High Temperature Flowing Afterglow	300–1800	
Critical points of water	647	$2.2 \times 10^7$
Laser-driven nanoshocks	600	$4 \times 10^9$
Sonochemistry	5000	$1 \times 10^8$
Diamond anvil cells		$5 \times 10^9$

Table 2. These methods, which expand the range of conditions under which reactions have been studied, have helped provide new insights into chemical reactivity, the role of internal energy in fostering reactivity, and the transfer of energy in molecular systems.

As simulations play an increasing role in the prediction of the behavior of complex systems, this drive to explore new ranges of experimental conditions is bound to increase rather than decrease. The potential danger of basing simulations on results extrapolated far beyond the range of conditions under which they were obtained has been frequently demonstrated. Thus, experiment and theory must move together to push out their frontiers. New experimental methods must be developed to probe systems in currently uncharted territory providing benchmarks for theory, and validating models that have been developed. And it is imperative that such models be based on a complete and well-tested understanding of the underlying fundamental principles.

The range of extreme environments under study is also bound to increase as more systems are treated by simulations in multidisciplinary efforts. From the chemistry of ignition and detonation of energetic materials at high temperatures and pressures, to chemistry in the cold, sparse interstellar medium, experimental and theoretical challenges abound. Challenges are also posed in the detailed chemistry occurring within materials under stress, as well as the interactions of materials with their environments. For example, simulations of the cracking of molecular materials requires accurate potentials for molecular bonds that are stretched well beyond their equilibrium conditions. Validating potentials in this region will be vital for ensuring confidence in such simulations.

Another increasingly important consideration in many simulations, the linking of information across multiple sets of time and length scales, presents another daunting set of challenges, particularly in nonequilibrium conditions where state-to-state dynamics plays an important role. Simulation methods based on modeling of molecular collisions are emerging that utilize the detailed chemical information that modern chemical physics can provide (see Chap. 3 of this volume by Boyd on Direct Simulation Monte Carlo methods). Given the high dimensionality of the problem, however, even these most detailed particle-based models require considerable simplifying assumptions. Simulations of combustion, or the interaction of objects with reactive high speed flows will have to couple chemistry with fluid dynamics. Particle-based models of such environments must reconcile time

scales from femtoseconds for chemistry to seconds for flow effects. It will be critical to develop tractable methods that retain the essence of the important details of chemical dynamics in these coupled models.

Pushing chemistry into new environments has often resulted in some surprising results. While developing methods to explore these new areas presents challenges, they also present opportunities. Already, new synthetic methods have grown out of exploration of chemistry in extreme environments. We must remain poised to take advantage of such new possibilities as they arise from studies of extreme environments.

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