

## 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		$5 \times 10^9$