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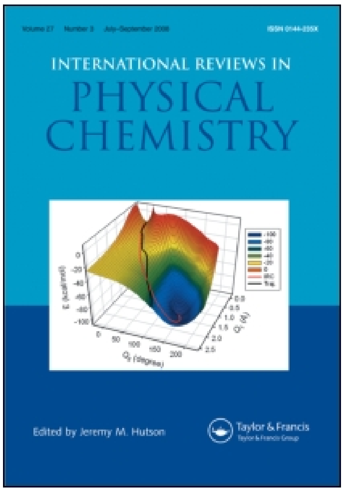

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Drawing by Zdenek Herman

Michael Henchman, Dynamic Explorer

This Festschrift honours a widely admired colleague, exemplary in his zeal and earnest dedication to research, teaching, and citizenship, as well as in his charm, wit, and intense humanistic interests. Many aspects of ion–molecule gas-phase chemistry have been shaped or enhanced by his vision and incisive analysis. Both in his own research and in major, definitive review articles, he has particularly fostered interdisciplinary perspectives. Thereby he has contributed fruitful new ideas to a remarkable range of domains. These include collision dynamics, solution chemistry

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and biochemistry in the gas phase, the radar signature of rockets, isotope exchange reactions, suprathermal organic chemistry, deuteration of exotic molecules in interstellar space and its cosmological implications, and the interrelationship of kinetics, thermodynamics, and the reaction hypersurface. It is apt that the 16 articles contributed to this special issue likewise attest to many fresh, inviting vistas of modern physical chemistry.

What follows is a quick sketch of Michael Henchman's scientific odyssey, largely gleaned or appropriated from his own writings. Often we quote him directly as well as citing pertinent papers from his publication list, which now spans nearly four decades.

Michael, on behalf of the host of scientists that cherish your friendship and inspiration, we are delighted to convey birthday greetings. We happily anticipate future opportunities to express our esteem by celebrating your further adventures and inimitable reports from the frontiers.

Hot atom chemistry

In the late 1950s, when MH began his research, he was captivated by the fledgling field of collision dynamics. It was a time of evangelical fervour, aroused by the prospect of new experimental methods capable of examining the actual molecular mechanics of gas phase reactions. Such was the nuclear-recoil technique employed by Richard Wolfgang at Yale to study high-energy chemistry. MH became his third graduate student and showed, for the first time, how a reaction mechanism could change markedly with energy [2, 3]. At low energies, collisions lasted long enough for the atoms to act in concert, allowing a tetrahedral target molecule to turn inside out, like an umbrella in a gale. At high energies, collisions were abrupt and localized, single atom striking single atom, like billiard balls on a pool table.

Beam studies of mechanism

Since the nuclear recoil technique permitted no direct control of the energy, MH switched to the study of ion–molecule reactions, where the energy could be controlled by an electric field. He learned new techniques: pulse techniques from Victor Talrose in Moscow in 1963, high-pressure mass spectrometry from Frank Field in Leeds in 1963/64 (spending a sabbatical there on a Guggenheim), and beam techniques from Wolfgang at Yale in 1965. These enabled MH to develop a new *multiple-pulse* technique to study reaction rates and mechanisms at low energies [15]. As he put it: 'We were able to explore if reactions proceeded by complex or direct mechanisms (that is to say, long-lived or fly-by)'. His review [13], written for a Faraday Discussion, has since been reprinted in the *Benchmarks of Physical Chemistry* series. Applied to electron-transfer reactions, the technique showed, for the first time at low energy, the extent of 'electron-jump' mechanisms [17, 21].

When developed further to span a greater energy range, the technique showed the energy dependence of three competing mechanisms for the reactions: $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ [20]. Recent studies, using modern flow-tube [53] and crossed-beam [56] techniques, confirm the earlier study, even though the *multiple-pulse* technique has now been superseded. MH has faithfully revisited this reaction for 30 years, using new methods as they have been developed. Although historically the first ion–molecule reaction to be studied, it is, as an open-shell system, exceedingly complicated. The combination of quantum chemistry with many experimental techniques, including flow-tube, ICR, molecular beam, photoionization, and supersonic expansion methods, has now yielded results from which a comprehensive picture has begun to emerge [53].

During 1965–1975, when beam-type kinetics were MH's primary interest, he wrote several reviews. A chief aim, seemingly oblivious to others at that time, was to integrate results from the neutral beam studies and the ion beam studies [8, 22, 24]. Another aim was to correlate ionic reactions in the gas phase and solution [22]. In a 160-page review [23], MH analysed critically for the first time the techniques available for measuring rate constants and cross-sections, and their interrelationship, as well as theoretical predictions for the results. Graduate courses at several universities have since used that review as a canonical text.

Solution chemistry in the gas phase

Around 1975 MH's interests expanded from high energy chemistry to solution chemistry: 'At Brandeis, three outstanding colleagues who were studying chemical reactions in solution—Ernest Grunwald, William P. Jencks and Kenneth Kustin—caused me to ask new questions. How could our detailed studies of collisions in the gas phase help the understanding of reactions in solution?' Most of chemistry and biochemistry occur in solutions rather than in the gas phase. Yet solution reactions cannot be directly studied in molecular detail because the solvent intrudes. 'Could the gas phase studies provide a new way?'

Adventitiously, David Smith and Nigel Adams developed at Birmingham about this time a new technique, the Selected Ion Flow Tube (SIFT). MH visited there in the summer of 1978 and again for a sabbatical year in 1980/81 to learn the technique [27]. Back in Massachusetts, MH's collaborators at the Air Force Geophysics Laboratory, John Paulson and Al Viggiano, duplicated the apparatus. Over the past decade, they have used it extensively for studies of 'solution chemistry in the gas phase'. The SIFT technique can stick one, two or three solvent molecules onto the reacting molecules in the gas phase, making what might be called a 'microsolution'. This enables study of what happens as the extent of the solvation is varied, ranging from no solvent at all towards complete solvation.

The Geophysics Laboratory group was the first to show that, contrary to general expectation, the change from zero to complete solvation does *not* occur monotonically [33], i.e. clusters do not necessarily mediate between the unsolvated and the fully solvated situation. This result is now cited in standard textbooks. For many reactions, the addition of a few solvent molecules in the gas phase can stop reaction altogether, even though the same reaction occurs in solution. The studies of MH and his colleagues have elucidated the distinct roles of the 'solvation shell' and the more remote bulk solvent. By itself, the solvation shell can stop reaction; but the addition of the bulk solvent can then restore it. These solution studies in the gas phase also probed the structure of the transition state for proton transfer [38] and for nucleophilic displacement [39, 42].

In summary, MH wrote: 'We have studied reactions where we now have a complete understanding of what is occurring—from the situation in the gas phase, where there is no solvent, to that in solution, where solvation is complete. The gas-phase studies have yielded new insight into those in solution and *vice versa* [50]. Years ago, when I first gave a graduate course in chemical kinetics, the subject frustrated me. It consisted of two distinct parts—gas kinetics and solution kinetics—without any apparent connection. There had to be a connection but at that time there was not. Much of my work of the past decade has been directed to establishing that connection'.

These solvation studies were reviewed by MH for the 1988 Faraday Discussion on *Solvation* [51]. The extensive discussion at that meeting [52] acknowledged the relevance of gas-phase studies to solution reactions.

Biochemistry in the gas phase and the tracking of rockets

Pursuing solution reactions in the gas phase led MH to an interesting biochemical problem: the use of energy, from the 'burning' of food in the body, for muscle action. This was thought to involve the reactive intermediate PO_3^-. But he concluded that: 'This is false because we found PO_3^- to be stable and unreactive [35]'.

That striking result induced MH and his colleagues to undertake the first synthesis of HPO_3, one of the strongest acids, and to measure the strengths of the strongest acids, then an unsolved problem [40, 52, 65]. Further, they showed these so-called superacids to be the most effective scavengers of electrons known [41]. If injected into the exhaust of a rocket re-entering the atmosphere, these compounds could scavenge the electrons and quench the plasma in the rocket wake, thereby allowing radio communication during re-entry and altering the radar signature of the rocket. Large rockets would appear to be small; missiles could seem invisible. MH noted: 'Providentially, this diabolical application of our innocent work on 'gas phase biochemistry' (undertaken by the US Air Force) was terminated by the end of the Cold War. It shows how the applications of highly abstract research can never be predicted'.

Isotope exchange

The structure of reaction intermediates and transition states was the focus of the work of MH and his colleagues in Birmingham as well as with F. Howorka, W. Lindinger, and T. Märk at Innsbruck. The reactions examined ranged from the most elementary: $D^+ + H_2 \rightarrow H^+ + HD$ [28, 30] to the more complex, such as: $CH_5^+ + CD_4 \rightarrow CH_4 + CD_4H^+$ [31, 60]. Interesting and unexpected results emerged from these studies: (i) The jump time of the proton transfer in the intermediate, $CH_5^+ . CD_4 \rightarrow CH_4 \cdot CD_4H^+$, was measured as a function of temperature [31, 60]. (ii) The zero-point energy of CH_5^+ was determined (and subsequently confirmed theoretically by Pople) [31]. (iii) Isotope-exchange reactions provided an effective probe in solvation studies [27, 50]. (iv) isotope-exchange also revealed key features of reaction hypersurfaces [49, 53, 60], including substantial energy barriers to exothermic ion–molecule reactions that challenged current orthodoxy [49]. (v) Modelling isotopic fractionation as a function of temperature [54, 64] led to the exotic world of interstellar molecules.

Molecules in interstellar space: 'big-bang' chemistry

During the past two decades almost 100 molecules have been observed in the interstellar medium. Some, such as $HC_{11}N$, are so reactive that they have never been synthesized on earth. These species are made in space at temperatures approaching absolute zero, probably by ion–molecule reactions. MH's interest in interstellar molecules concerns a further intriguing aspect: they contain up to 1000 times more deuterium than molecules on the earth. This has cosmological implications, as the fraction of deuterium in the cosmos depends on its origin, whether it is open or closed.

MH has sought to determine how the interstellar molecules acquire deuterium. The reaction $D^+ + H_2 \rightarrow H^+ + HD$ was characterized as the first step in the chain of deuteration reactions [28]. Forbidden steps in that chain have been identified by distinguishing those reactions which show barriers from those that do not [49]. A model for the temperature dependence of isotope-exchange reaction rates [54, 64] has also been developed which is applicable as well to the deuterium content of interstellar clouds.

Physical organic chemistry at suprathermal energies

In collaboration with P. Hierl of the University of Kansas, MH has applied beam techniques to fundamental processes in physical organic chemistry, using the elevated energies to probe features of the reaction hypersurface, particularly for nucleophilic displacement [42, 51, 75]. This has provided new understanding of the competition between nucleophilic displacement and proton transfer [36]. Such an exemplary use of beam techniques to explore the upper reaches of the hypersurface deserves to be more widely appreciated and emulated.

Linking kinetics and thermodynamics to the reaction hypersurface

For MH, 'A central interest of my research in kinetics is the interrelationship of thermodynamics and kinetics' [28, 32]. This led him to promote and edit a panel discussion of *Entropy-driven reactions* [45]. Several of his experimental studies employ kinetics to probe the reaction hypersurface [28, 42, 49, 50, 51, 53, 54, 69]. He has shown that this provides a useful basis for comparing positive and negative ion–molecule reactions [24], and also for comparing ion–molecule reactions with radical–radical reactions [53, 69]. In several cases, he has inferred the principal features of the hypersurface from the structure of the reactants [49, 53, 60], for example identifying where exothermic reactions over a concave hypersurface may still show energy barriers [24, 49]. For this important concave case, he has also provided calculations of collisional cross-sections and rate constants [23, 44]. In an especially striking application of kinetic data, he has used it to show that standard heat of formation of the electron given in thermodynamic tables cannot be correct [55, 62].

The reaction $D^+ + H_2 \rightarrow H^+ + HD$ has been studied to seek basic understanding of one of the simplest prototypes; for example, this system shows clearly the relationship between statistical factors, symmetry numbers and reaction entropies [28]. The dissociative attachment process, $e^- + HX = H + X^-$, is another example where a simple reaction reveals a basic effect, in this case resulting from dramatic changes in the height of the centrifugal barrier [41].

An abiding thrust of this work has been to attain an inclusive, unifying overview of elementary processes in chemical kinetics [8, 16, 22, 23, 24, 51, 58, 67]. His most ambitious effort attempts a systematic treatment in terms of the structure of the hypersurface [69]; this is a major part of a book he is now writing with Joe Grabowski of the University of Pittsburgh.

Chemistry and art—A unifying interdisciplinary course

In his teaching, MH has also long strived to foster interdisciplinary perspectives and linkages. He avows that 'Ever since my student days, when I was caught up in the Snow/Leavis controversy over *The Two Cultures*, I have been challenged by the teaching of science to non-scientists and *vice versa*'. His first publication, as a graduate student, was on this topic [1]. Thirty years ago, as the Kelvin Lecturer for the British Association, he televised toy trains to demonstrate the collision mechanisms of elementary chemical reactions to the layman [16]. Another of his early popular lectures, dealing with symmetry and asymmetry, bears the gripping title, *Guts, Positrons, and the Origin of Life* [5].

In 1991, a grant from the Sloan Foundation challenged the faculty of Brandeis University to establish science courses for non-scientists. In response, MH developed a course in *Chemistry and Art* 'which uses art, familiar to the student, as a bridge to teach science to art students [72]. By seeing how science increases understanding and appreciation of art, the students see science in action and acknowledge its value'. Taught now in the regular curriculum to large classes of enthusiastic students, MH's course has attracted attention outside the university. At present, he gives 'about 20 presentations a year, in the US and abroad, to universities, colleges, high schools, alumni groups, parents, to departments of science, art and education, to national meetings of scientific and conservation societies'. He also serves as an educational consultant in interdisciplinary courses to other institutions. This fall he taught a workshop for high-school teachers and students at the Kalamazoo Advanced Science and Mathematics Center, and this Spring will give a NSF Chautauqua course at Harvard. He has been invited to organize a symposium of speakers from Europe and the US on *Art Restoration* for the biennial meeting on Chemical Education to be held at Clemson University next August. In this way, he is literally giving new meaning to chemical dynamics!

Currently, MH is engaged in an intriguing historical study, tracing how the blossoming of chemistry in the first half of the nineteenth century influenced the development of European painting, particularly how early work on transition metal coordination compounds was utilized by precursors of the Impressionists.

BRETISLAV FRIEDRICH
Harvard University
ZDENEK HERMAN
Heyrovsky Institute
DUDLEY HERSCHBACH
Harvard University

Born in 1935 in London (under the sign of *Pisces*), MH was educated at Sherbourne School and Clare College, Cambridge. In 1956, he voyaged to the New World, to earn a doctorate at Yale. In 1960 he did a postdoctoral at Cambridge, and after a few years teaching at Leeds, returned in 1967 to America to join the faculty at Brandeis. The drawing (by Zdenek Herman) includes motifs of MH's many-faceted life in New England.

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Honours

1953–56	Huish Exhibitioner, State Scholar, Major Open and Foundation Scholar, Clare College, Cambridge, UK
1956–59	Mellon Fellowship, Yale University
1960–61	Science Research Council Fellowship, Cambridge University, UK
1963	Royal Society/USSR Academy of Sciences Exchange Fellowship at the Institute of Chemical Physics, Moscow
1967	Kelvin Lecturer, British Association for the Advancement of Science
1980–81	United Kingdom Science Research Council Senior Visiting Fellowship, University of Birmingham, UK
1981	National Academy of Sciences/Czechoslovak Academy of Sciences Exchange Visitor, J. Heyrovsky Institute, Prague
1984–86	Air Force Systems Command Visiting Professor, Air Force Geophysics Laboratory
1986	Brotherton Research Lecturer and Visiting Professor, University of Leeds
1988	Fulbright Professorship, Institute for Ion Physics, University of Innsbruck, Austria
1990–91	Alexander von Humboldt Senior Research Prize, held at the University of Göttingen