Benton Seymour Rabinovitch. 19 February 1919 — 2 August 2014

Charles T. Campbell and Ruth A. Rabinovitch

originally published online March 16, 2016

---

**Supplementary data**

"Data Supplement"
http://rsbm.royalsocietypublishing.org/content/suppl/2016/03
/15/rsbm.2015.0021.DC1

**Email alerting service**

Receive free email alerts when new articles cite this article -
sign up in the box at the top right-hand corner of the article
or click [here](http://rsbm.royalsocietypublishing.org/subscriptions)
BENTON SEYMOUR RABINOVITCH
19 February 1919 — 2 August 2014
BENTON SEYMOUR RABINOVITCH

19 February 1919 — 2 August 2014

Elected FRS 1987

BY CHARLES T. CAMPBELL¹* AND RUTH A. RABINOVITCH

¹Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA

Benton Seymour Rabinovitch was one of the pioneers of chemical dynamics. His brilliant experiments performed during his four decades as a Professor of Chemistry at the University of Washington in Seattle provided most of our early quantitative measurements of the efficiency with which energy is transferred between molecules in gas-phase molecule–molecule collisions and in collisions of molecules with solid surfaces. More importantly, his work provided quantitative estimates of the rates with which vibrational energy deposited locally within a molecule is redistributed among the many vibrational modes within that molecule, proving that the equilibration of this vibrational energy among these modes almost always occurs in approximately one picosecond. He further showed that this validates (in most cases) the assumptions of Rice–Ramsperger–Kassel–Marcus (RRKM) theory. He also developed several widely used mathematical shortcuts for using RRKM theory to make important predictions about physical chemistry. These shortcuts greatly increased both the applications and impact of RRKM theory, so that it has become one of the most important theories of physical chemistry. It continues to guide much of our fundamental understanding of chemical dynamics and reaction kinetics even today. In addition to being a great scientist, Seymour Rabinovitch was a devoted husband and father. He raised four accomplished children, and later in life became an expert in the art of silversmithing, a writer of children’s books, and a philanthropist. His offspring are following beautifully in his footsteps in their kindness to fellow human beings, their excellence in scholarship, science and art, and in their energetic dedication to improving the world through teaching, research, service and philanthropy. The same can be said for his academic offspring as well.

* charliec@uw.edu (corresponding author)
Biographical Memoirs

EARLY YEARS

Benton Seymour Rabinovitch was born in Montreal, Canada, on 19 February 1919, the youngest of the seven children of Rochelle (née Schacter) and Samuel Rabinovitch. Rochelle came to Canada as a teenager from Botosani, Romania, and in Montreal met her future husband, Samuel, who had emigrated from Bessarabia (now part of Moldova and the Ukraine). Seymour was raised by devoted parents and six elder siblings, all of whom provided moral and financial support during his education; he was the only one among them to receive an advanced degree.

At five years of age, Seymour declared that he wanted to be a lawyer, advance to Prime Minister, and be seated to the right of the King of England. During his sophomore year in high school, he was taught by his chemistry teacher, Mr Aiken, that at a temperature of zero kelvins all matter would disappear. Seymour found this concept so intriguing that he changed his career direction to chemistry.

Seymour attended the Strathcona Academy, in the Montreal suburb of Outremont. After the depression hit and the family’s real estate business foundered, Seymour would watch his father leave the house each morning to try to find odd jobs to provide food for his family. His two brothers, for their part, left high school to help support the family and ensure that Seymour could continue his education. Seymour became fluent in French, because many of the courses attended by the English-speaking children in Quebec were taught in this language. He loved poetry and memorized a tremendous amount of it, entertaining himself and family with recitations. As a youth, he also enjoyed playing chess, making a name for himself as a young champion on the Montreal street park scene and continuing to play until the last months of his life.

Seymour entered McGill University in 1936 as a second-year student majoring in chemistry (figure 1). Although his studies kept him busy, he also found time for membership in clubs devoted to social problems and to the peace movement. He earned his Bachelor of Science degree in chemistry in 1939, with first-class honours (figure 2). While in college, Seymour lived at home, walking more than three miles each way; he spent the summer months selling magazines to businesses and homes in Montreal’s environs, helping fund his education; he served as a crew leader during his last year. During weekends in winter he enjoyed skiing, the physical benefits of this activity being enhanced considerably by the lack of tow lifts on the ski slopes.

Montreal neighbourhoods were often separated by ethnicity, such as Jewish or Italian. There were some areas from which Jews were excluded, such as Mount Royal. Discriminatory practices that were applied in residential areas gradually disappeared after World War II, as did certain ethnicity-based university policies affecting student admissions and faculty life. When Seymour entered college, a quota system governing the admission of Jews to McGill was still in force, which meant that he needed a near ‘A’ average in high school to be admitted. The same quota system applied to the medical and professional schools, which troubled Seymour greatly and left a lasting impression upon him. He remained a strong advocate of minority rights throughout his life.

PhD studies and service during World War II

Shortly after Canada entered World War II (on 10 September 1939, a week after Britain), Seymour received a letter from the Dean of the Graduate School of McGill University enjoining him to stay with his original plan of commencing doctoral studies, pointing out
Figure 1. At the laboratory bench, Biology Building, McGill University, in 1939.

Figure 2. Graduation in 1939: BSc in chemistry, McGill University.
that the department’s energies would be directed towards research that contributed to the war effort. Seymour duly entered graduate school in autumn 1939 and completed his PhD with Professor Carl Winkler in February 1942 (figure 3), shortly before Rudy Marcus, a fellow student also in Winkler’s laboratory. Seymour’s thesis was entitled ‘Studies in chemical kinetics (academic research) and the detection of vesicants (war research)’. Although chemical kinetics became his life’s work, a detour during the war years into the field of vesicant detection was his contribution to the Allied war effort. Seymour initially entered the Chemical Warfare Laboratory in Ottawa as a civilian, but in December 1942 he went to a training camp for officers at Gordon Head, in Victoria, British Columbia. In 1943 Seymour was sent to England as a captain in the Canadian Army, remaining there until 1946 (figure 4). He was stationed first at Leatherhead with training at two chemical warfare establishments, one at Porton Down in Wiltshire and a second near the border with Scotland.

While in London as a Jewish officer, Seymour received hospitality from the family of Harry and Yetta Clifford, enjoying meals and family life and forming a lifelong friendship. During this period he developed a simple colorimetric method for detecting the presence of mustard gas by impregnating cloth swatches with appropriate dyestuffs or resin and placing them on battlefields or clothing. These were to be inspected early on a day of troop advancement. This method was an outgrowth of Seymour’s PhD research and yielded excellent results. After the war, Seymour was sent to Washington DC to participate in a US National Chemical Panel on War Research, where he presented his work on chemical warfare. Throughout his life he savoured the memory of being asked, ‘Hmmm, Rabinovitch … do you have anything to do with the guy who invented the mustard gas detector?’

On 12 June 1944, Seymour’s unit was posted to Portsmouth. At the end of July, more than a month after D-day, they landed in Courseulles-sur-mer, France. He recalled digging slit
trenches, three feet long, to accommodate a camp cot, conceding that most of the actual spade work was done by his batman. After St Lô was captured, Seymour’s unit advanced rapidly to Ghent, followed by Antwerp, Breda, Tilburg, Leiden, Raubkammer bei Münster, and Apeldoorn. He led a team of young scientists who investigated German munitions factories and battlefields as the Germans retreated, looking for violations of the Geneva Convention on Weaponry. In Raubkammer bei Münster, his unit was the first to enter the German command centre where manufacturing and experimentation had been done. Fluorophosphate esters and nerve gases were among the substances they found.

**Postdoctoral studies**

After the war, Seymour taught physical chemistry to former soldiers at the Khaki College, the Veterans Rehabilitation College of Canada, situated in Watford, England. He was awarded Milton and Royal Society of Canada fellowships, enabling him to conduct postdoctoral studies in physical chemistry at Harvard University, under Professor George Kistiakowsky. It was at this time that he began to date his future wife, Marilyn Werby of Boston (figure 5).

**Four decades as professor at the University of Washington**

In 1948 Seymour joined the Department of Chemistry at the University of Washington, where he remained throughout his academic career. He and Marilyn had a long-distance engagement and married in 1949, making Seattle their home. He attained the rank of full professor there in 1957.
Seymour felt strongly that to not form lifelong friendships with one’s graduate students was a lost opportunity. He formed lasting attachments to these students, who numbered 41 over the course of his career. He also mentored some 60 postdoctoral and visiting faculty associates. He and Marilyn greatly enjoyed hosting parties for the graduate students and postdoctoral researchers, occasionally also organizing large festive summer weekend reunions in Seattle. Seymour and Marilyn’s marriage of 24 years was loving and full. Together they shared the joys of raising four children: Peter, Ruth, Judith and Frank, all of whom went on to have successful careers of their own. Their family enjoyed two sabbaticals: one in Ottawa in 1962, and a second at Oxford, during 1972. They also took several car trips across America and Canada in their station wagon, visiting friends and relatives. Marilyn’s untimely death from cancer in 1974 was a tremendous loss and bereavement; Seymour was fortunate in having several of his children living with him or nearby during this period. In January 1980 he married Flora Reitman of Montreal, and together they enjoyed 34 years of loving marriage, pursuing many shared interests, which included travel, long walks and collecting antiques. They purchased a flat in London in the early 1980s, spending several months there every year. Seymour and Flora helped establish a graduate student space in Bagley Hall, the University of Washington Chemistry Building. Rab’s Room, as it was affectionately called, was envisioned as a place for refreshments, the exchange of ideas, and the development of friendships and camaraderie among graduate students. Rab’s Room owed its inspiration to similar facilities that Seymour had been impressed by during his sabbatical in England.

Seymour taught and conducted research at the University of Washington for four decades. During his career he became a virtuoso of experimental physical chemistry; his work provided the first experimental verification of important theories of molecular dynamics and energy transfer within molecules in the gas phase. A brief summary of his research contributions

Figure 5. In 1947 with his fiancée, Marilyn, at a beach party in or near Boston given by his postdoctoral advisor at Harvard University, Professor George Kistiakowsky.
Benton Seymour Rabinovitch

while at the University of Washington is provided below. Altogether, he co-authored more than 230 scientific papers as well as a widely used book on physical chemistry. He retired as Professor Emeritus in 1986, although he continued to come in regularly ‘to work’ for another 20 years. During those later years he had many important roles, including advising and mentoring young faculty, serving as a role model, and engendering warm personal interactions among the faculty, students and staff. One of us (C.T.C.) benefited tremendously from these interactions and will remain forever grateful to have enjoyed them, although he deeply regrets not having taken greater advantage of his opportunities to spend time with Seymour.

Seymour received numerous awards for his scientific contributions, including the American Chemical Society’s 1983 Peter Debye Award and the 1984 Polanyi Medal bestowed by the Royal Society. He was elected a member of the American Academy of Arts and Sciences in 1979 and a Fellow of the Royal Society in 1987. In 1991 he received an honorary Doctorate of Science from the Technion – Israel Institute of Technology, in recognition of his extraordinary work in the field of reactions and intermolecular energy transfer dynamics. He served as an editor for *Journal of the American Chemical Society* and was Chairman of the Division of Physical Chemistry of the American Chemical Society. In 2005 the University of Washington established the B. S. Rabinovitch Endowed Chair of Chemistry in his honour. Seymour and his students made such extensive use of and contributions to RRKM theory that, when Professor Rudolph A. Marcus was awarded the Nobel Prize in Chemistry in 1992, he joked that Seymour was the missing R in RRKM. He also invited Seymour and his wife Flora to attend the week of festivities and celebration in Stockholm (figure 6).

Figure 6. Seymour Rabinovitch with his wife Flora attending the 1992 Nobel Award Dinner, as guest of Rudolph A. Marcus, recipient of the 1992 Nobel Prize in Chemistry. (Online version in colour.)
Seymour became a Professor at the University of Washington in 1948 and continued publishing scientific papers from there until 1990. The major foci of his research during those 42 years were: (i) unimolecular reaction kinetics, (ii) intermolecular energy transfer, (iii) intramolecular energy relaxation and (iv) energy transfer when molecules collide with solid surfaces. These topics resulted from his deep interest in the rates and kinetics of chemical reactions, particularly for elementary reaction processes. This interest dated back to his research for his PhD dissertation under the direction of Carl Winkler, which involved the study of bimolecular reaction kinetics. Bimolecular reactions are reactions that result from the collision between two molecules to produce products, shown schematically as
\[ A + B \rightarrow C + D. \] [1]

The rate for such an elementary reaction is typically proportional to the concentrations of each reactant, \([A]\) and \([B]\):
\[ \text{rate} = k(T)[A][B]. \]

The temperature dependence of the rate constant generally follows the Arrhenius Law,
\[ k(T) = \nu \exp\left(-\frac{E_{\text{act}}}{RT}\right), \]
where \(E_{\text{act}}\) is the activation energy or activation barrier to reaction. As Seymour stated in his dissertation, according to ‘Lewis’s fundamental formulation’, the rate of such a bimolecular reaction can also be expressed as
\[ \text{rate} = Z_{AB} \exp\left(-\frac{E_{\text{act}}}{RT}\right), \]
where \(Z_{AB}\) is the number of A–B collisions per unit time (which is also proportional to \([A][B]\)) and where \(\exp\left(-\frac{E_{\text{act}}}{RT}\right)\) is ‘the Boltzmann expression for the fraction of collisions in which the joint energy along the line of centers exceeds \(E_{\text{act}}\)’.

At the University of Washington, Seymour turned his attention to the presumably simpler case of gas-phase unimolecular reactions, of the general class
\[ A \rightarrow \text{product(s)}. \] [2]

Here again the rate can be expressed as proportional to the concentrations of each reactant with a proportionality or rate constant, \(k(T)\), that follows the Arrhenius Law,
\[ \text{rate} = k(T)[A] = \nu \exp\left(-\frac{E_{\text{act}}}{RT}\right)[A]. \]

However, this reaction becomes more complicated than bimolecular reactions when one tries to understand how the reactant gets to a high enough energy to exceed the activation barrier. It still needs a collision to activate \(A\) above the energy barrier, \(E_{\text{act}}\). Seymour’s early work asked the question: How exactly does that happen?

Instead of being a single elementary step as implied by the reaction equation \(A \rightarrow \text{products}\), it requires three steps, hence its added complexity:
\[ A + M \rightarrow A^* + M \quad \text{(excitation)}, \] [3]
\[ A^* + M \rightarrow A + M \quad \text{(de-excitation)}, \] [4]
where M can be another molecule of A, any bath gas, or a solid surface, and the asterisk signifies a molecule that has been excited to an energy state higher than average. These three elementary steps highlight the areas of his most important research contributions. The first two steps refer to *intermolecular energy transfer*; that is, the transfer of energy between molecules (or between a molecule and a solid) in gas-phase collisions. The last step involves *intramolecular energy relaxation*, wherein the excess energy in molecule A denoted by the asterisk (which starts out highly localized in a part of A) redistributes itself within that molecule, so that it can break or rearrange chemical bonds to give the product(s).

His experiments were marked by brilliant research design, whereby he simplified a problem to its barest essential ingredients. As an example, consider his 1955 study of the kinetics of cis–trans isomerization reactions of olefins, one of the most important and commonly studied classes of reactions in organic chemistry. To simplify its study, he chose as the reactant trans-dideuteroethylene (1)*, which is absolutely the simplest example of this entire class of reactions:

\[
\begin{align*}
\text{D} & \quad \text{H} \\
\text{C=C} & \quad \rightarrow \quad \text{C=C} \\
\text{H} & \quad \text{D} \\
\end{align*}
\]

Ethylene is the smallest olefin, and the only difference between reactants and products is the swapping of the location of one of the two D atoms for one of the two H atoms from the trans to the cis location across the C=C double bond. Because D is an isotope of H, the product is nearly identical to the reactant, with negligible change in the electronic structure upon reaction, and the product has nearly the same energy as the reactant. It thus provided the easiest case to model theoretically using a combination of quantum mechanical and statistical mechanical calculations. He proved this to be a homogeneous, unimolecular reaction and determined a high-pressure limit with a true activation energy \(E_{\text{act}}\) of 65 kcal mol\(^{-1}\) and a frequency factor \(\nu\) of \(10^{13}\) s\(^{-1}\). He showed these values to be consistent with calculations using quantum mechanics, transition state theory and statistical mechanics. This set a high standard for depth of understanding in the kinetics of organic chemical reactions.

Similarly, Seymour performed many experiments that were very cleverly designed to critically test proposed theoretical models for intermolecular energy transfer—that is, reactions [3] and [4] above—thus showing which models worked best, as well as the ranges of validity of their intrinsic assumptions (8). As an example of his approach in this area and the intensity of his efforts, let us examine how he addressed the crucial question: How does the efficiency of energy transfer in an A–M collision depend upon the choice of M, the so-called ‘bath gas’? To this end, he studied the kinetics of isomerization of methyl isocyanide using 109 different inert bath gases (4). As shown in figure 7, he found that the relative activation–deactivation efficiency per collision, \(\beta_c\), increased with the boiling point of M up to a saturation value of unity (corresponding to full energy equilibration upon a single collision). From this he concluded that attractive nature of the A–M interaction is important. Indeed, he found that polarizability, dipole moment and H-bonding ability of the bath molecule all increased efficiency. These experiments provided some of the earliest

* Numbers in this form refer to the bibliography at the end of the text.
support for the very important realization that such collisions involve the formation of a transient A–M complex, whose lifetime increases with the strength of A–M attraction. He also concluded that efficiency increases in general with the number of transitional modes of the collision complex (which increases with the number of atoms in the A–M complex). Closer inspection of figure 7 shows that he found three subcorrelations, namely for (i) monatomic, (ii) diatomic and linear, and (iii) complex nonlinear molecules, reflecting the importance of dynamical considerations associated with the conservation of angular momentum in the energy transfer process.

Seymour next addressed the last step in this three-step unimolecular reaction mechanism (steps [3] to [5] above): $A^* \rightarrow \text{product(s)}$. He asked: Once the reactant A is excited by a collision with M, what specifically happens before it delivers its products, and, if given options as to what those products might be, how do the details of this energy redistribution within the molecule A determine which products are made? This involves the very important general topic known as intramolecular energy relaxation. Through a series of very clever experiments, he proved unequivocally that highly excited reactive polyatomic molecules behave ergodically (that is, statistically) in this respect, at least on timescales longer than ca. 1 ps. He also found the first exceptions to this, which require extremely fast reactions that occur with a characteristic time constant near $ca. 10^{-12}$ s (that is, very similar to the rate of internal energy randomization) or faster.

This question of ergodicity asks: Is newly deposited energy in molecule A distributed among all the modes of the molecule’s internal motion with equal probability by the time its reaction occurs, or is this energy more localized to the part of the molecule where it originated? Ergodic behaviour is the basic assumption of RRKM theory (1951–52) and is also inherent in transition state theory (albeit in a much less general way); his elegant proof of this concept therefore had a huge impact on research in physical chemistry and chemical physics, and one that is still important today.
To prove the assumption of ergodicity, he invented an approach called ‘chemical activation’, whereby the excited A* molecule is not produced by a collision with M, but instead by an exothermic association reaction that simultaneously forms and excites A. In this way, energy can be deposited very locally into a specific chemical bond. If the excitation level is above the critical threshold for reaction, $E_{\text{act}}$, then a unimolecular reaction to some other product(s) may occur:

$$A^* \rightarrow P. \quad [7]$$

In competition with this, the excited molecule may deactivate upon collision with a bath gas, M, thus quenching it to levels below $E_{\text{act}}$, resulting in the stabilization of the initial product, A. The first use of the method was reported in 1960 by Harrington, Rabinovitch and Hoare (2), with the main purpose of studying the efficiency of collisional deactivation (that is, step [4] above). Seymour later showed that by increasing the pressure of M and its collisional energy transfer efficiency (as in figure 7), he could tune the speed of such collisional deactivation, and thereby use it as a clock to time the events that happen in step [5]—the evolution of A* to another product or products.

By choosing the chemical activation reaction that produces A*, he was able to controllably place the resulting excitation energy at different bonds in the molecule (9). A schematic example is shown in figure 8.

In another important example, he studied the addition of the CD$_2$ diradical to the C=C double bond in hexafluorovinylcyclopropane to produce a highly excited bi-cyclopropane that is totally symmetric except for its D isotopic substitutions on one side (5):

$$\text{F} - \text{C} - \text{C} - \text{C} = \text{C} + \cdot \text{CD}_2 \rightarrow \text{F} - \text{C} - \text{C} - \text{C} - \text{F}. \quad [8]$$
This excited molecule then decomposes quickly to liberate CF₂ either from the same end of the molecule,

\[
\begin{align*}
F & \quad F \\
\text{CH₂} & \quad \text{CD₂}^* \\
\end{align*}
\rightarrow
\begin{align*}
F & \quad \text{C} = \text{C} \quad \text{+} \quad : \text{CF}_2, \\
\text{CH₂} & \quad \text{D} \\
\end{align*}
\tag{[9]}
\]

or from the other side,

\[
\begin{align*}
F & \quad F \\
\text{CH₂} & \quad \text{CD₂}^* \\
\end{align*}
\rightarrow
\begin{align*}
F & \quad \text{C} = \text{C} \quad \text{+} \quad : \text{CF}_2. \\
\text{CD₂} & \quad \text{H} \\
\end{align*}
\tag{[10]}
\]

He differentiated these products by measuring the location of its D, whether on the double bond or in the cyclopropane part. If the energy deposited by the CD₂ addition remained localized to that end of the molecule, only direct reaction to the former product, reaction [9], would be expected. In contrast, nearly equal amounts of both products [9] and [10] were actually observed, indicating that the extra vibrational energy is statistically redistributed throughout the whole molecule first, before this decomposition reaction occurs. By increasing the pressure to generate more frequent collisions with bath gas, quenching the initially excited molecule and preventing its reaction, he set a clock on this reaction’s time. Because he knew the rate of quenching by a bath gas from his intensive studies of intermolecular energy transfer (see above), he was able to prove that it occurs in less than \(10^{-10}\) s.

In a later study, he increased the bath-gas pressure further and found that the fraction of product from reaction [9] increased at very high pressures until more than 25% of the total product corresponded to reactants whose internal excitation remained near its original location (6). He explained this by recognizing that the initial non-randomly excited reactant was quenched by collisions, but this molecule also had a second chance for quenching after internal energy randomization. This additional quenching reaction is not available on the direct route to non-random product via reaction [9], so its relative yield increases with bath gas pressure. If the rate constants for internal energy randomization and non-random product formation are known, this variation is predictable from modelling of this multi-step kinetic competition. By finding values that fitted the data, he determined the rate constants for internal energy randomization and non-random product formation to be \(ca. 1.1 \times 10^{12} \text{s}^{-1}\) and \(ca. 3.5 \times 10^{11} \text{s}^{-1}\), respectively (6).

To our knowledge, this was the first study to prove that some chemical reactions indeed occur before internal energy randomization, and the first study to measure the rate constants for such a kinetic competition and thereby the quantitative extent to which it competes with internal energy randomization. This classic experiment is discussed in chemical reaction dynamics courses today as a first step towards state-selected chemistry (for example Chemistry 762 when taught by Professor F. Fleming Crim at the University of Wisconsin – Madison).

Later, in similar studies using the chemical activation technique on various fluorocarbons and hydrocarbons that extended to higher pressures (shorter times), he showed that the statistical redistribution of vibrational energy throughout the whole molecule generally occurs within \(ca. 10^{-12}\) s (9, 11).
In discussing these results, he introduced the idea of the ‘characteristic time constant for local vibrational energy to distribute throughout the molecule’, a concept that guides much of our thinking about chemical dynamics today. Thus, he deduced internal energy relaxation times with a model whereby he assumed that a vibrational subset (moiety) of the radical is initially excited, and that its excess energy decays exponentially with time in a manner crudely characterized by a single time-independent average relaxation constant \( \tau \) (11, 12). He ultimately concluded that ‘relaxation times (\( \tau \)) of magnitude less than 10\(^{-12} \) s signify the applicability of statistical methods, such as RRKM theory, for the calculation of unimolecular rate constants of magnitude below 10\(^{12} \) s\(^{-1} \).’

Some raised the question of whether the rate of this intramolecular energy relaxation process might be much slower if probed at much lower excitation levels where intermode coupling mechanisms may be weakened. To test this, he measured the rates of intramolecular vibrational energy relaxation in systems that reacted at much lower levels of excitation (43 kcal mol\(^{-1} \)) than previously studied (110 kcal mol\(^{-1} \)), using the technique of state selection by chemical activation, and found similarly fast times (11). Others raised the possibility that a heavy atom, through inertia, might block internal energy transfer in excited species. He investigated this by a chemical activation study of 4-(trimethyl lead)-2-butyl and 5-(trimethyl tin)-2-pentyl radicals, prepared and excited by the reaction of H atoms with the corresponding 1-olefins (13). Again, energy randomization among the vibrational modes was found to occur on a subpicosecond timescale (less than 10\(^{-12} \) s) in all the radicals studied.

Seymour’s studies validated RRKM theory and showed when it might break down. This understanding is now central to all of physical chemistry and chemical physics! He even coined the name ‘RRKM theory’. In his own papers, he cited as the advent of this theory two papers from Rudolph A. Marcus (Marcus & Rice 1951; Marcus 1952). The 1992 Nobel Prize in Chemistry was awarded to Marcus ‘for his contributions to the theory of electron transfer reactions in chemical systems’, for which RRKM theory provided an important conceptual foundation.

Seymour also developed several widely used mathematical shortcuts for applying RRKM theory to make important predictions about reaction kinetics, chemical dynamics and other aspects of physical chemistry. These shortcuts made RRKM calculations much easier to conduct, and greatly increased both the applications and the impact of RRKM theory. RRKM has become one of the most important theories of physical chemistry, guiding much of our fundamental understanding of chemical dynamics and reaction kinetics even today. Many papers have used his ‘Whitten–Rabinovitch (WR) approximation’ (3) when doing the vibrational energy-level sums needed for RRKM calculations. Even more have used his approximation for the evaluation of internal energy-level sums and densities that include anharmonic oscillators and hindered rotors (7). Indeed, these two theoretical works are his most highly cited papers!

Seymour also studied the transfer of energy when gas molecules collide with solid surfaces. He pioneered the ‘variable encounter method’ involving the study of the relaxation of an initial vibrationally cold ensemble of molecules into a vibrationally hot distribution by a known and variable number of successive collisions with a hot wall (10). He used reactions such as the ring opening isomerization of 1,1-cyclopropane-d\(_2\) to propene, measuring the reaction probability per reactant-molecule collision with walls of increasing temperature for reactors of different lengths, as shown in figure 9.

From such experiments, he determined that a steady-state population of vibrational energy levels at the surface temperature is reached in a small number of collisions (10–20) even at high surface temperatures, and that this decreases towards a single collision at low
temperature. This increase in the efficiency of energy transfer at lower surface temperature was early evidence that molecules at low temperature experience temporary trapping on the surface followed by desorption, and that they establish a Boltzmann population of energy levels corresponding to the surface temperature in their transient lifetime on the surface, now commonly referred to as ‘trapping–desorption’ encounters (with unit sticking probability). He showed, for example, that such vibrational accommodation is complete in one collision for cyclobutene at temperatures below 425 K on Pyrex and seasoned silica surfaces, and at temperatures below 550 K on seasoned gold surfaces (14).

In summary, the research of Seymour Rabinovitch and his group at the University of Washington has had a huge positive impact on the course of physical chemistry research worldwide. It led us into the modern era of chemical dynamics and provided many of its most basic concepts. Given the importance of chemical dynamics and kinetics in energy and environmental technologies, and indeed in all aspects of chemical industry, his research has been of tremendous benefit to mankind. His mentoring of graduate students, postdoctoral associates and younger faculty also made an equally important contribution to the greater scientific community. He did all this while always maintaining a wonderful gentlemanly nature. His kindly nature even came through in his papers, in which he often acknowledged a referee for helpful suggestions.

**POST-RETIREMENT YEARS: SILVERSMITH, WRITER OF CHILDREN’S BOOKS, AND PHILANTHROPIST**

While on sabbatical in England with Marilyn and the children in 1971, Seymour became interested in learning about silversmithing, silver patinas and the science of Sheffield silver.
Benton Seymour Rabinovitch

His interest began during a search for a silver anniversary present for his brother: he had bought a piece of what he believed to be old Sheffield, only to discover later that it was instead electroplated. He decided to continue the search for a genuine piece and gradually became intrigued with the culture of English antiques shops and silver merchants, and with the history of English silver more generally. He started collecting antique fish and cake slices, enchanted with the varied adornments of piercing, chasing and engraving and the different shapes. What had begun as a modest collection of slices from the eighteenth and nineteenth centuries broadened after Marilyn’s death, and he became an ardent collector, acquiring pieces in the USA, Britain and Europe. The slices satisfied his aesthetic sense and had the added advantage of being small, easy to store and not as costly or as difficult to transport as hollowware. At the same time, he felt that his new hobby required something more, and he decided that, besides collecting the pieces, he would also study the evolution of their patterns and forms. His earliest slice was made in 1723, and he carried his investigations through to the end of the nineteenth century, eventually conducting scholarship on silver of the twentieth century, an area with relatively little documentation. Seymour authored three books on silver servers: Antique silver servers for the dining table (16), Contemporary silver (19), co-authored with Helen Clifford, and Contemporary silver, part II: recent commissions (20). He wrote scholarly pieces on the chemistry of silver patinas, including ‘A new method for gilding silver: use of organic gold sols’, published in Metalsmith (17), ‘The look of antique silver’, in Silver Magazine (18), and ‘The patina of antique silver: a scientific appraisal’, in Silver Society Journal (15).

Seymour later began taking lessons in silver working, to learn at first hand how pieces were made; he went on to design and create a broad-bladed server himself. After getting to know several silversmiths, he decided to make a study of contemporary work, and in the late 1980s began commissioning the creation of contemporary servers. In so doing, he had two objectives in mind: first, to provide support, in a modest way, for independent silversmiths and the craft; and second, to make a comparative study of contemporary styles in metalsmithing relating to one particular type of object: the broad-bladed server. In 1995 an exhibition titled ‘Slices of silver’ held at Goldsmiths’ Hall in London introduced to the public a mesmerizing collection of 42 sterling silver fish servers and cake slices created by contemporary British and American silversmiths. The collection consisted entirely of pieces commissioned by Seymour over a 20-year period and showcased the skills and artistic diversity of these contemporary silversmiths. He developed a close rapport with each artist, always encouraging freedom of creative expression. Seymour continued to sponsor new pieces, resulting in the growth of his collection to more than 100 items.

Over the years, Seymour’s collection has been exhibited at the Winnipeg Art Gallery, the National Ornamental Metal Museum in Memphis, the Seattle Art Museum, the Schneider Art Museum in Ashland, Oregon, the Aberdeen Art Gallery in Scotland, the Nottingham Castle Museum and Art Gallery, and Goldsmiths’ Hall. Seymour’s collection and his passion for craftsmanship became the subject of magazine articles, including ‘Fish get a slice of the action’, published in Country Life, ‘Slices of silver’, in Winnipeg Art Gallery Tableau, May/June 2003, and ‘On collecting’, in Silver Magazine. He was an invited speaker at New York University’s ‘Sterling Modernities’ conference in 2002, giving a presentation on broad-bladed slices. In 2005, through the American Friends of the Victoria and Albert Museum, Seymour donated the entire collection to this London landmark, where it resides today.

Seymour was a member of the Silver Society (London) and the American Academy of Arts and Sciences. He was honoured with the National Metallsmiths Hall of Fame award, and was
named by *Silver Magazine* as a ‘world personality in silver’. In 2000 he was inducted into the Worshipful Company of Goldsmiths, London, as an Honorary Liveryman—a rare honour for someone not born in the UK.

Seymour’s passion for collecting led to the exploration of many small towns in Britain and America with his wife Flora, the search for new treasures becoming part of the daily adventure of travel. His passion for collecting influenced his children, all of whom appreciate art and antiques. He established a memorial endowment at the University of Washington School of Arts’ Metal Design Program in Marilyn’s memory, to recognize and encourage the work of young metalsmiths.

Growing up with four older sisters and two brothers, Seymour had little opportunity to cook as a boy. However, while raising his children he enjoyed dabbling in the kitchen. His recipe ‘Boiled can: a delectable caramel sauce’ was included in *But the crackling is superb, an anthology on food and drink by Fellows and Foreign Members of the Royal Society* (Kurti & Kurti 1997).

In recent years, Seymour authored a children’s storybook entitled *Higgledy piggledy: a tale of four little pigs* (21), based on an original tale he used to tell his children when they were young. In the introduction, ‘What’s in a name?’, and in his story, he illustrated the themes of facing challenges in life and treating others kindly, and the importance of showing resourcefulness in difficult situations.

Seymour led an extraordinarily rich and productive life, one of abiding devotion to his family and his work. He died at his home in Seattle on 2 August 2014 at the age of 95 years, surrounded by his family. His memory is a continuing inspiration to friends and family, and his
generosity, warmth, philanthropy and charm are cherished. He is survived by his wife Flora, children Peter (wife Jacqueline), Ruth (husband Thomas), Judith (husband Tim), Frank (wife Karen), stepchildren Howard (wife Ramona) and Ellen Reitman, twelve grandchildren and three great-grandchildren (figure 10).

ACKNOWLEDGEMENTS

C.T.C. gratefully acknowledges Professor Fleming Crim for helping him to understand the scientific papers and contributions of B. S. Rabinovitch. The authors thank Professor Paul Hopkins and Stephanie Hemmingson for proof reading the manuscript, and a reviewer for helpful comments.

The frontispiece photograph was taken in about 2000 (photographer unknown).

REFERENCE TO OTHER AUTHORS

Kurti, N. & Kurti, G. (eds) 1997 But the crackling is superb, an anthology on food and drink by Fellows and Foreign Members of the Royal Society. Bristol: Adam Hilger.


BIBLIOGRAPHY

The following publications are those referred to directly in the text. A full bibliography and curriculum vitae are available as electronic supplementary material at http://dx.doi.org/10.1098/rsbm.2015.0021 or via http://rsbm.royalsocietypublishing.org.

(8) 1977 (With D. C. Tardy) Intermolecular vibrational energy transfer in thermal unimolecular systems. Chem. Rev. 77, 369–408.
(9) 1979 (With I. Oref) Do highly excited reactive polyatomic molecules behave ergodically? Accts Chem. Res. 12, 166–175.


(16) 1991 *Antique silver servers for the dining table. Style, function, foods and social history.* Northampton, MA: Joslin Hall.


