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In Memoriam: Jean-Pierre E. Grolier (1936–2022)

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On January 26, 2022, Professor Jean-Pierre E. Grolier passed away peacefully in his home in Clermont-Ferrand, Auvergne, France, after fighting valiantly, for more than 2 years, against a rare neuromuscular disorder. His wife Geneviève and their two children, Pierre-Stanislas and Marie-Edith, were at his side. Jean-Pierre Grolier was born in Constantine, Algeria, on December 22, 1936, but in the wake of the Algerian War, the family was expelled, as were many other European settlers (ca. 1,000,000 *pieds-noirs*), to mainland France.

Jean-Pierre Grolier began his scientific career with an M.S. degree (*Licence-ès-Sciences*, 1961) in General Chemistry from the *Université de Clermont II* (later renamed *Université Blaise Pascal*, UBP) in Aubière, near Clermont-Ferrand, France, and continued his studies at this university to receive a Ph.D. degree (*Docteur-ès-Sciences*) in Physical Chemistry in 1970, his supervisor being Professor André Viallard. In parallel, rising through the ranks, in 1962, he was made a *Maître-Assistant* in the Chemistry Department of the University of Clermont II, and a *Maître de Conférence* in 1971. In 1983, he became a Full Professor (Department of Chemistry) and he retired in 2007 (after chairing the Department for several years), but remained as Emeritus Professor for another decade, that is, from 2007 until 2018, when he finally withdrew from all activities in the Department. During his career, Jean-Pierre Grolier supervised 75 PhD dissertations and master's theses, and welcomed numerous visitors from abroad, i.e., students, post-docs, and scientists/collaborators. Honoring his five decades of dedication to thermodynamics, on April 15, 2019,

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Professor Karine Ballerat-Busserolles [Institut de Chimie de Clermont-Ferrand, *Université Clermont Auvergne* (UCA), formerly known as *Université Blaise Pascal*)] organized "calo2019: Calorimetry and Thermal Analysis—A journey dedicated to Professor Jean-Pierre Grolier" at UCA.

Even in the early days of his career in physical chemistry, Jean-Pierre Grolier's enthusiasm for establishing international scientific collaborations was evident, a characteristic trait that remained an important part of his personality throughout his life. For instance, during 1972–1973, he was a Postdoctoral Fellow in George C. Benson's Thermochemistry Laboratory (*National Research Council of Canada*) in Ottawa, Canada, and again, in 1977, he stayed with G. C. Benson as Visiting Scientist. In 1973, he was a Visiting Scientist with Patrick Picker at the *Université de Sherbrooke* (Sherbrooke, Quebec, Canada), and the years 1974–1977 he spent as Research Associate at the *Centre de Recherches de Microcalorimétrie et de Thermodynamique* (CRMT/CNRS, Calvet-Tian Institute) in Marseille, France. During 1979–1980, Jean-Pierre Grolier was a Fulbright Visiting Professor at the Chemistry Department, *University of Delaware*, in Newark, Delaware, USA, with Robert H. Wood, and in 1983, he returned as a NATO Fellow. In 1981, he spent some time as a Visiting Scientist with Loren G. Hepler at the Chemistry Department of the *University of Lethbridge*, Alberta, Canada, and renewed his contact with Loren at the Department of Chemistry of the *University of Edmonton*, Alberta, in 1985.

Fittingly, Jean-Pierre Grolier and I, Emmerich Wilhelm [then at the Institut für Physikalische Chemie (Institute of Physical Chemistry), IPC, *Universität Wien* (University of *Vienna*)], first met in 1971 in Orono, Maine, USA, at the combined 26th Calorimetry Conference & 2nd International Conference on Thermodynamics and Calorimetry (subsequently, this IUPAC-endorsed biennial conference series was renamed and became the International Conference on Chemical Thermodynamics, ICCT). A few years later, after some preliminaries, Jean-Pierre Grolier, Henry Kehiaian (both were then working at CRMT/CNRS in Marseille) and I agreed to start a broadly based scientific cooperation (experiment *and* theory) focusing on selected thermodynamic properties of liquid nonelectrolyte mixtures, that is, on excess molar volumes V^{E}, excess molar enthalpies H^{E}, excess molar heat capacities C_P^{E} at constant pressure, and related properties: Henry Kehiaian nicknamed it the TOM (*Thermodynamics of Mixtures*) project. Years before, that is in 1967, he had already been invited to Wien (Vienna), Austria, to the IPC, by Friedrich Kohler (my PhD mentor) and me. In fact, this had been Henry's first trip from Poland [Institute of Physical Chemistry, *Polish Academy of Sciences*, Warszawa (Warsaw)] to the "west" ! Following Jean-Pierre, as experimental bases of our work, we selected the then novel, cutting-edge techniques known as (I) vibrating-tube densimetry for determining densities and, thus, excess volumes, and (II) Picker calorimetry: since his stay with Patrick Picker, Jean-Pierre had seen the enormous potential of these techniques [1, 2] and had become thoroughly acquainted with these types of flow microcalorimeters. I had met Picker the first time at the 3rd ICCT in Baden near Vienna, Austria, 3–7 September 1973. In 1994, he was the recipient of the *James J. Christensen Memorial Award* of the American Calorimetry Conference, presenting an Award Lecture entitled "What is Happening in Flow Calorimetry?" In addition, Setaram, France, a manufacturer and global supplier of high-performance instruments for calorimetry and thermal analysis, had offered Jean-Pierre the opportunity to test prototypes of Picker-type calorimeters *for free*. Hence, in the summer of 1975, Jean-Pierre, Henry, and I officially initiated our scientific collaboration within the Austrian-French Program on Scientific-Technical Cooperation in Marseille, France, at the CRMT/CNRS. I still remember vividly our intensive work in the laboratory, the focused discussions, and the relaxed yet stimulating atmosphere at our dinners in selected restaurants,

such as the garden restaurant at Marseille's main train station *Gare Saint-Charles*, at "*Ma Verte Campagne*" or at "*L'Entrecôte*" at the *Vieux Port*. Additional early members of our "thermodynamics research group," who contributed significantly to the scientific output, were Americo Inglese from the *Istituto di Chimica Fisica*, *Università di Bari*, Bari, Italy, and Mohammad H. Karbalai Ghassemi, later known as Mohammad H. Hamedi, from Iran, who received his Ph.D. degree in Marseille in 1977 (in the 1980s, he became Professor of Mechanical Engineering at the *K.N. Toosi University of Technology* in Tehran, Iran, was Dean of the Faculty of Mechanical Engineering, and Vice President and President of the University; he retired in 2018). In 2003, he "returned to the roots" and spent a sabbatical period with Jean-Pierre at UBP in Clermont-Ferrand.

After transferring all the laboratory equipment (by private car, that is, with a Mustang Grande!) to Jean-Pierre's home university in Aubière/Clermont-Ferrand (it is situated in the Auvergne, the central region of France, about 500 km north of Marseille, and is the hometown of the well-known *Michelin* tire company), since 1978 experimental work continued at the *Université Clermont II* (later renamed *Université Blaise Pascal*), capably and reliably supported by Alain H. Roux and Geneviève Roux-Desgranges. A few years later, Henry Kehiaian, already *Directeur de Recherches*, moved from Marseille to Paris (the city of his dreams) to work at the *Institut de Topologie et de Dynamique des Systèmes* (ITODYS/CNRS): thus, the *research triangle* Clermont-Ferrand—Paris—Wien (Vienna) was established and remained operative for the next three decades. In fact, in the late 1970s and in the 1980s, based on the "Picker flow-technique," Jean-Pierre's laboratory became *the* internationally leading research center for the determination of excess heat capacities at constant pressure of liquid mixtures with unparalleled precision. Of particular note is the determination of C_P^{E} of the liquid mixture $\{\text{benzene}\,(x_1) + \text{cyclohexane}\,(x_2)\}$ at 298.15 K and atmospheric pressure: it was measured with an imprecision characterized by a standard deviation from the selected Redlich–Kister fitting equation of $\pm 0.025\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (which is less than 1% of the maximal $\left|C_P^{\mathrm{E}}\right|$), thus strongly supporting the use of this system as a *test mixture* for calorimetric measurements of excess heat capacities of binary liquid nonelectrolyte systems [3].

Altogether, I spent about 6 years in France, predominantly in Clermont-Ferrand, and Jean-Pierre was a frequent visitor at the IPC in Wien (Vienna). For *28 years,* our collaborative research was funded via bilateral peer-reviewed research grants (for 2 years each) within the Austrian-French Program on Scientific-Technical Cooperation: to the best of my knowledge, it was the *longest* continuously funded collaboration ever, resulting in more than 80 scientific articles, book contributions, and reports, in numerous posters, oral presentations, invited lectures, and plenary lectures. Some of the scientific articles Jean-Pierre considered to be most characteristic of our cooperation are listed as Refs. [3–15], with reviews focusing on excess heat capacities and excess volumes being provided by Refs. [16, 17]. Note that Ref. [7] reports the *first W-shaped* $C_{\mathrm{P}}^{\mathrm{E}}(x)$ curves ever (*two* minima and *one* maximum), while a (weakly) *M-shaped* $C_P^{\mathrm{E}}(x)$ curve (*two* maxima and *one* minimum) was found for the mixture $\{(1-x)\mathrm{H_2O} + x\mathrm{CH_3COOH}\}$ [5]. *M-shaped* excess molar enthalpies $H^{\mathrm{E}}(x)$ are reported in Ref. [13]. I still remember the animated discussions of some of these novel results Jean-Pierre and I had with Donald Patterson (*McGill University*, Montreal, Quebec, Canada) in Clermont-Ferrand, focusing on the importance of *random*/*nonrandom* contributions to $H^{\mathrm{E}}(x)$ of liquid nonelectrolyte solutions [18, 19]. They came about because during summer, he and his wife, Geneviève Delmas, occasionally visited her family home situated only about 50 km south of Clermont-Ferrand. On December 15, 2016, Donald Patterson passed away at the age of 89,

To further international research cooperation, Jean-Pierre participated in an early *Erasmus* network (focusing on chemical thermodynamics/physical chemistry of the liquid state) that included colleagues in Germany (R. N. Lichtenthaler, Physikalisch-Chemisches Institut, *Universität Heidelberg*, Heidelberg, see Ref. [20]), Spain, UK, and Austria (E. Wilhelm, Institut für Physikalische Chemie, *Universität Wien (Vienna)*, see Ref. [13]). In addition, within the *Erasmus Program*, in 2006 and 2007, he taught courses on *Thermal Methods* (2nd year Master level) at the *University of Aberdeen*, UK.

Throughout his career, Jean-Pierre loved to travel extensively, be it by car or by airplane, to attend conferences/symposia and science-related workshops, and to interact with fellow scientists, thereby initiating many important research connections. These activities, in combination with the general thermodynamic expertise reflected by the publications originating in Marseille and subsequently in Clermont-Ferrand, and the steadily increasing number of available cutting-edge experimental techniques, made his laboratory (*Laboratoire de Thermodynamique*, for short) a magnet in the field of chemical thermodynamics for colleagues as well as young aspiring scientists from all over the world as far as Japan [21–33]. The large number of TOM-inspired cooperations with Spanish scientists has certainly stimulated/influenced research in chemical thermodynamics in Spain [5, 10–12, 23–25, 27, 28].

Major driving forces for progress in instrumentation are the desire (I) to increase the area of applicability, that is, for instance, to cover larger temperature and pressure ranges, or to study new kinds of systems, (II) to improve precision and accuracy of the experimental methods used, and (III) to increase the speed of measurements. Indeed, over the years, in Jean-Pierre's laboratory, several new/improved types of instruments, covering important areas of thermodynamics, were developed.

One of the most important experimental techniques introduced during the last decades is known as *scanning transitiometry* [34–47]. It is *the* hallmark of the longstanding French-Polish collaboration that started in the early 1990s between Jean-Pierre E. Grolier and Stanisław L. Randzio (Institute of Physical Chemistry, *Polish Academy of Sciences*, Warszawa (Warsaw), Poland), and included, in addition, Jaques R. Quint (also from *Laboratoire de Thermodynamique*, UBP), and somewhat later, Miroslaw A. Chorążewski (Institute of Chemistry, *University of Silesia*, Katowice, Poland). This technique has been successfully used to determine isobaric thermal expansivities $\alpha_P = V^{-1}(\partial V/\partial T)_P$, isothermal compressibilities, $\beta_T = -V^{-1}(\partial V/\partial P)_T$, isochoric thermal pressure coefficients $\gamma_V = (\partial P/\partial T)_V = \alpha_P/\beta_T$, isochoric molar heat capacities C_V, and isobaric molar heat capacities C_P of liquids at pressures up to 700 MPa, and over wide temperature ranges (up to 500 K). Of particular interest is the observation that for many simple liquids there exists a *crossing point* of the α_P-isotherms at elevated pressures. Consider, for instance, α_P -isotherms for liquid *n*-hexane [37] between 253.15 and 503.15 K: below (62 ± 2) MPa, α_P *increases* with increasing temperature, while for higher pressures, α_P *decreases* with increasing temperature. Jean-Pierre E. Grolier and Stanisław L. Randzio were co-inventors of this technique and hold several patents.

The collaboration with Robert H. Wood on using high-temperature and high-pressure flow techniques to measure densities and heat capacities started in 1979 (see above) and led to the transfer of these versatile technologies from Newark to Clermont-Ferrand. Jean-Pierre valued Bob's wise counsel: nick-naming the resulting experimental techniques the *Calvet-Picker-Wood cocktail*, he used them for developing improved instruments for measuring heat capacities of gases and liquids, for determining heats of mixing of fluids at flow conditions, and for the simultaneous measurement of heats of mixing and densities of mixtures at superambient conditions [48–56]. As succinctly expressed by Jean-Pierre [57], Bob

Wood became an *Auvergnat de coeur et de science* and was honored with the title *Doctor Honoris Causa* (*Dr. h.c.*) of the Université Blaise Pascal in 1997. A few years later, in 2006, I too was honored with the title *Dr. h.c.* from UBP. Interestingly, I first met Bob at the *same* conference where I had first met Jean-Pierre, that is, in Orono, Maine, USA, 12–14 July 1971; and since then I had the pleasure to meet Bob on many occasions at international conferences [58], at the University of Delaware in Newark, at the University of Wien (Vienna), Austria, and, perhaps most enjoyable, during leaves of absence at UBP in Clermont-Ferrand: he too enjoyed his stays in the Auvergne greatly! Bob passed away on February 3, 2019, at the age of 86.

Isothermal titration calorimetry (ITC) has been developed to measure the heat of reaction resulting from a binding process between two (or more) species in solution and is in use since the 1960s. During the last decades, however, the sensitivity of the instruments used has *greatly* improved, thereby allowing application of this technique in a large variety of fields, notably in biochemistry and biophysics, in biology, and in drug discovery. In fact, there is a steady rise in the number of ITC relevant publications, thus making periodical critical surveys/reviews highly desirable [59–67]. ITC was one of the last experimental techniques adopted in Clermont-Ferrand and provided much of the basis of the French-Mexican collaboration, centering on José Manuel del Rio (*Instituto Mexicano del Petróleo*, Ciudad de México, México).

Although most of Jean-Pierre's scientific work focused on nonelectrolyte systems, the collaboration with Glenn T. Hefter (Chemistry Department, *Murdoch University*, Murdoch, Western Australia) represents an excursion into the field of *electrolyte solutions*. At 25 °C, apparent molar volumes and isobaric apparent molar heat capacities for NaCl, LiCl, NaF, KI, sodium tetraphenylborate ($NaBPh_4$), and tetraphenylphosphonium chloride (Ph_4PCl) dissolved in aqueous solutions containing up to 40% by mass *t*-butyl alcohol have been determined by flow densitometry and flow microcalorimetry, respectively [68]. Analogous measurements were reported in Ref. [69] for NaCl, KCl, KNO_3, $AgNO_3$, KI, $NaBPh_4$, and Ph_4PCl dissolved in acetonitrile (AN)–water mixtures containing up to $x_{AN} = 0.25$. Volumetric properties of, and ion pairing in, aqueous solutions of Na_2SO_4 and K_2SO_4 have been reported at temperatures ranging from 298 K to 573 K, and for pressures up to 30 MPa, in Ref. [70]. An analogous study reports densities and apparent molar volumes of NaF and KF, respectively, dissolved in water at temperatures ranging from 25 °C to 354 °C, and at pressures up to 30 MPa [71]. Jean-Pierre visited Glenn several times "down under."

Investigation of the thermophysical properties of polymers, in particular at elevated temperatures and pressures, and identification of optimal operating conditions in polymer synthesis and (industrial) polymer modifications and transformations through different processes, such as foaming, were topics Jean-Pierre became interested in rather late in his career [72–82]. The main coworkers during this period of his scientific life were Florin Dan, from the Macromolecular Chemistry Department, *Gh. Asachi Technical University*, Iasi, Romania, who later moved on to become Research Scientist (Core R&D, Analytical Sciences) with *The Dow Chemical Company* at Midland, MI, USA, Séverine A. E. Boyer, who is now with MINES Paris Tech, *PSL Research University*, Sophia Antipolis, France, and Hirohisa Yoshida, from Urban Environmental Science, *Tokyo Metropolitan University*, Tokyo, Japan. In fact, over the years, interaction with Japanese colleagues at both the professorial level (for instance, to name but a few, Profs. Suga, Yoshida, Kimura, Ogawa, Murakami, Nakazawa, Saito, Takagi) as well as via accepting post-docs from Japan, has played an important role in the scientific development of the laboratory at UBP. In turn, Jean-Pierre visited Japan frequently: for instance, he attended Japanese Conferences on Calorimetry and Thermal Analysis (JCCTA), he visited the *Research Center for Thermal*

and Entropic Science in Osaka (current Director is Prof. Yasuhiro Nakazawa), he participated at the 14th ICCT in Osaka (1996), the 26th International Conference on Solution Chemistry in Fukuoka (1999), and the 21st ICCT in Tsukuba (2010). At the latter conference, the Japanese Emperor and Empress joined the Conference Reception, and Jean-Pierre and his wife, Geneviève, had the honor and pleasure to directly participate in the welcoming of the Royal couple—a rare experience indeed!

Towards the end of his career Jean-Pierre became interested in the thermodynamic investigation of properties of fluids in *confined* spaces [83–88]. In collaboration with Valentin Eroshenko [89] and Yaroslav Grosu (both from the Laboratory of Thermomolecular Energetics, *National Technical University of Ukraine*, Kyiv, Ukraine), and Jean-Marie Nedelec (Institut de Chimie de Clermont-Ferrand, *Université Clermont Auvergne*, formerly UBP), experiments focused on systems consisting of a porous material (metal organic frameworks, such as the exceptionally stabile Zeolite Imidazolate Frameworks, ZIFs [90]) and water as a non-wetting fluid. High-pressure intrusion–extrusion of water into hydrophobic porous solids is a promising technology to store, release, or transform mechanical energy (leading to shock-absorbers and molecular springs).

Professor Grolier's scientific oeuvre comprises more than 280 scientific articles in refereed journals and book chapters, and 5 patents. His name is also associated with over 500 conference contributions, which number includes 47 Plenary Lectures and 78 Invited Lectures.

In addition to his university position, Professor Jean-Pierre Grolier held many offices in professional organizations. Nationally, he was influential in the *Association Française de Calorimétrie et d'Analyse Thermique* (AFCAT), internationally, he was a member of *Commission I.2* (*Thermodynamics*) of IUPAC (1985–2001), was President (2002–2008) and Past President (2008–2010) of the *International Association of Chemical Thermodynamics* (IACT), and Vice President (1999–2018) of *Eurostar Science*, *European Society for Applied Physical Chemistry*. He particularly valued being a member of the *Board of Directors* of the *American Calorimetry Conference*, in which position he served 1989–1991 and again from 2000 onwards. He regularly attended the annual Calorimetry Conferences (and the joint meetings with the JCCTA in the Turtle Bay Resort on Oahu, Hawaii), always looking forward to participating in, and contributing to, an excellent technical program, amidst a suitable setting, and to meeting old friends and colleagues for discussing scientific issues and general ideas. To recognize Professor Grolier's contributions to thermodynamics, an honorary symposium entitled "Five Decades of Scientific Discovery" was organized at the 74th Calorimetry Conference (CALCON 2019) in Santa Fe, at the Hilton Santa Fe Buffalo Thunder, New Mexico, USA, July 28–August 2, 2019—it was the last pre-COVID-19 conference. Chair: Professor Richard D. Sheardy, Department of Chemistry and Biochemistry, *Texas Woman's University*, Denton, Texas; Program Chair: Professor David P. Remeta, and Secretary-Treasurer: Professor Conceição A. Minetti, both from the Department of Chemistry and Chemical Biology, *Rutgers—The State University of New Jersey*, Piscataway, New Jersey). In his Plenary Lecture, Jean-Pierre discussed *Working Bodies Composed of a Lyophobic Nanoporous Matrix and Non-wetting Fluid*. My contribution to this honorary symposium was on *Excess Properties of Binary Liquid Mixtures: A Success Story*, the focus being on topics we had investigated together. Sadly, this conference in Santa Fe was the last time we met in person.

Professor Grolier's scientific achievements were acknowledged by several awards/honors:

– *Calvet Prize* (AFCAT, 1985);

– *Honorary Member* (Polish Association for Calorimetry and Thermal Analysis, 1991);
– *Świętosławski Medal* (Polish Association for Calorimetry and Thermal Analysis, 1994);
– *Kurnakov Medal* (Russian Academy of Sciences, provided by the Kurnakov Institute of General and Inorganic Chemistry, 1994);
– *Commander's Cross of the Order of Merit of the Republic of Poland* (Poland, 1995);
– *Hugh M. Huffman Memorial Award* (American Calorimetry Conference, 1997);
– *Applied Chemical Thermodynamics Prize* (Swiss Association for Calorimetry and Thermal Analysis, 1998);
– *F. D. Rossini Award* (IUPAC/IACT, 2004);
– *-Mège Prize* (Académie des sciences, belles-lettres et arts de Clermont-Ferrand, 2005);
– *AICAT-SETARAM Award* (Italian Association for Calorimetry and Thermal Analysis, 2008);
– *Officer*, *Academic Palms* (France, 2008).

In the 80s and 90s, my wife Olga and our daughter, Katja Dagmar, frequently visited me in Clermont-Ferrand during summer (I usually rented an apartment in Chamalières, only a few kilometers away from Jean-Pierre's home). I treasure the warm hospitality of Jean-Pierre and his wife, Geneviève, during these scientifically and socially so memorable times. On a larger scale, I always enjoyed the receptions in their garden (weather permitting), that was/is a green island harmonizing beautifully with their elegant house on Boulevard Lavoisier.

At the young age of 52, Americo Inglese passed away in 1998. Our old friend Henry Kehiaian passed away at the age of 80 in 2009, and Jean-Pierre and I published an obituary in the *Journal of Chemical & Engineering Data* [91] and in *Fluid Phase Equilibria* [92]. Now Jean-Pierre Grolier has left us at the age of 86. The Funeral Mass was celebrated at the church *Notre-Dame de Chamalières*, and its musical frame was selected by Jean-Pierre himself *pour un jour spécial*. The three pieces of music by Fryderyk Chopin, Wolfgang Amadeus Mozart, and Antonín Dvořák, respectively, reflect his longtime relation with Poland, Austria, and America, and with friends and colleagues therefrom. The collegial fraternity of thermodynamicists (of many fields), will miss him dearly: we will miss his science input and inquisitive mind, his helpfulness and generosity, his personal charm and *joie de vivre*, in short, his friendship.

Jean-Pierre, you lived a long and successful life, you were a wonderful friend, and you will be fondly remembered. *Requiescat in pace*.

Last greetings,

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