Philosopher-Scientists at the Interface of Physics and Chemistry: Paneth and Polanyi on Chemistry as an Exact Science

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Many historians and philosophers of science have addressed historical and epistemological questions about the relations between chemistry and physics.[1] Eric Scerri is among philosophers who have argued that theoretical chemistry cannot be reduced to the theoretical physics of quantum mechanics, and others, including chemists such as Stephen Weininger, Roald Hoffmann and Pierre Laszlo, have discussed the existence of distinctly chemical concepts such as molecular shape, aromaticity, steric effects, strain, and reactivity.[2] Recently R. J. Snooks has suggested that a difference between chemistry and physics is physicists' use of thought experiments. Snooks argues that, in contrast to physics, chemistry does not exhibit universal laws that originate in *a priori* reasoning and are open to thought experiments.[3]

On several occasions, Scerri has brought attention to the role in chemical philosophy of the physical chemist Friedrich Adolf Paneth (1887-1958). Fritz Paneth's historical and philosophical papers were collected in a 1964 volume edited by Herbert Dingle, and Paneth was profiled by Klaus Ruthenberg in a 1997 essay on "philosophising chemists" in the journal *HYLE*.[4] Paneth was a colleague of another philosophising chemist, Michael Polanyi (1891-1976), who also has been profiled in *HYLE* and whose anti-positivist writings on the personal and practical character of scientific knowledge are well-known among philosophers and sociologists of science since the 1960s. As with Paneth, the earliest of Polanyi's philosophical writings date back to the 1930s.[5]

For the physical chemists Paneth and Polanyi, the practice of chemistry had a great deal to do with the instruments, mathematical methods, and explanatory theories of physics. Their own chemical research depended on the pioneering work of physicists such as Ernest Rutherford and Niels Bohr, and, at a more personal level, on collaboration with physicists such as Georg von Hevesy, Fritz London,

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and Eugene Wigner. Paneth and Polanyi shared in their attitudes toward the relation between physics and chemistry an emphasis on the irreducibility of the behavior of chemical compounds to merely the properties of atoms, and a conviction of the inexactitude and flexibility of chemical rules and laws in comparison to physical theories. In what follows, the first discussion concerns the professional interactions between Paneth and Polanyi, and then there follow a few examples of their characterisations of the relations between chemistry and physics.

Chemical Careers

In 1931 Fritz Paneth gave a public lecture on chemical epistemology to the Gelehrte Gesellschaft of Königsberg. The lecture was published immediately in the Society's *Schriften* and much later, in 1962, it was translated into English for the *British Journal of the Philosophy of Science* by Paneth's son, the physicist and philosopher Heinz Paneth, also known by his Anglicised name, Heinz Post.[6] The Austrian-born Fritz Paneth received his doctorate in chemistry in Vienna and became in 1912 an assistant to Stefan Meyer at the Institut für Radiumforschung. Paneth taught in Vienna, Prague, and Hamburg, and he then had appointments in Berlin from 1922 to 1929 and in Königsberg from 1929 to 1933, when he was forced to leave Germany because of his Jewish origins. In England, Paneth had appointments at Imperial College in the University of London. He moved to the University of Durham in 1939. He led the chemistry division of the Joint British-Canadian Atomic Energy Team in Montreal during wartime and returned to Germany in 1953, to the Max Planck Institute in Chemistry in Mainz, after his mandatory retirement at Durham. Paneth is perhaps best known in chemistry for his demonstration in 1929 of the existence of the methyl free radical, using a lead mirror (or film) technique, and for his lifelong work in radiochemistry, including his early pioneering research in Vienna, in collaboration with Georg de Hevesy, using radioactive isotopes in tracer experiments.[7]

Michael Polanyi was born in Budapest, where he completed a medical degree in 1913 and a Ph.D. thesis in physical chemistry in 1919. He studied physical chemistry in Karlsruhe in 1912 with Georg Bredig and Kasimir Fajans, and he briefly returned to Karlsruhe in 1919 after political events forced him to leave his position at the University of Budapest where he was Hevesy's assistant in physical chemistry. Polanyi moved to the Kaiser Wilhelm Institute for Fiber Chemistry in Berlin in 1920, and he became director of the chemical-kinetics research group in Fritz Haber's Institute for Physical Chemistry and Electrochemistry in 1923. Anti-Semitism forced Polanyi to leave Germany in 1933, and he settled at the

University of Manchester, first as Head of Physical Chemistry, and later, from 1948 to 1952, as Professor of Social Studies. In physical chemistry, Polanyi's researches focused on the adsorption of gases on solid surfaces, including a quantum mechanical approach to adsorption which he developed with Fritz London, x-ray diffraction studies of natural fibers and metals, and chemical kinetics, including Polanyi's development with Henry Eyring of what came to be called the "semi-empirical method" for predicting transition states and activation energies for chemical reactions.[8]

Polanyi and Paneth may have first met at an April 1920 meeting of the Bunsengesellschaft in Halle, and they were friends in the 1920s in Berlin.[9] Polanyi had been involved in an earlier debate on the nature of chemical isotopes between Fajans in Karlsruhe and Paneth and Hevesy in Vienna. Fajans and Hevesy each had done research in Ernest Rutherford's laboratory in Manchester, and Paneth first met Hevesy in Rutherford's laboratory in 1913.[10] Paneth spent the summer term of 1913 in Frederick Soddy's laboratory in Glasgow at the time that Soddy was coining the term "isotopes" for atoms having differing atomic mass and the same atomic number, the concept of atomic number having been just established by George Moseley. Collaborating in Vienna, Paneth and Hevesy in 1914 took Soddy's position that different isotopes of the same atomic number were chemically identical rather than just very similar, exhibiting what Paneth and Hevesy called *Vertretbarkeit,* or the facility of replacing each other, in crystallisation and in electrochemical reactions. Fajans, then in Karlsruhe, disagreed and included among his arguments against the chemical identity of isotopes some thermodynamic arguments that he got from an unpublished paper by Polanyi, predicting that two substances of different atomic weight would have different free energies.[11] Polanyi learned from Hevesy that Hevesy and Paneth planned a reply to Fajans, and Polanyi suggested to Fajans that Hevesy, Paneth and Fajans compose a joint paper. Instead, separate articles appeared, with the view of Hevesy and Paneth winning out by the early 1920s, after research by Francis Aston and others made clear that there are many more isotopes than just the radioactive ones that had been discovered first.[12]

Philosophical Reflections

As with the discovery of isotopes, many developments in physics and chemistry in the early decades of the twentieth century highlighted the question of the relations between the practices and epistemologies of chemistry and physics. In his Königsberg lecture of 1931, Paneth drew upon his experiences in radiochemistry and in free-radical chemistry to discuss some fundamental chemical concepts in light of recent scientific results. He noted that mathematical statements often are not preferable or adequate in chemistry. Sodium chloride is salty, hydrogen sulfide smells bad, cinnabar is red, and gold is lustrous. Chemistry, he noted, referring to a description by Emil Fischer in Fischer's autobiography, is about "bangs and stinks." Physicists no longer speak of molecules and atoms as solid spheres, he said, but as mathematical relations in four-dimensional space. "But successes of chemistry often lie elsewhere", cautioned Paneth, "as in biological and historical sciences."[13]

Paneth reflected on the old conceptions of matter theory, elementary substances, and chemical transformations. How do elements persist in compounds? In what sense does the soft metal sodium and the poisonous green gas chlorine exist in colorless, crystalline table salt? How surprising is it, Paneth asked, that Spinoza was skeptical in the 1660s of Robert Boyle's demonstration that nitre may be synthesised from an acid and a base, which are substances of entirely different properties? A distinction must be made in chemistry, Paneth explained, between a simple substance, such as chlorine, that can be characterised by its qualitative properties and a fundamental, or transcendent, substance, such as chlorine, that persists in compounds as a substance without qualities. The atomic theory of Rutherford and Bohr lets us understand that the unchanged atomic nucleus constitutes the fundamental substance, while the optical, chemical, and other qualities of the simple substance have disappeared.[14] Paneth also attributed this distinction to Dmitri Mendeleev, noting that Mendeleev differentiated the "material constituent, not perceptible to the senses, of a composite body" from the "simple body as a single homogeneous substance."[15] Similarly, said Paneth in 1931, "the radicals of organic chemistry exist, *almost without exception*, in the world of the transcendental alone."[16]

One of the key differences between chemistry and physics, most certainly for Paneth and Polanyi, lay in this phrase "almost without exception." Polanyi made this point in a very brief letter of 1936 to the British journal *Philosophy of Science* a few years after he settled in Manchester and about the time that he found himself defending the semi-empirical approach of his transition-state theory against objections from physicists who demanded *ab initio* calculations for energy states.[17] "The subject of chemical concepts as opposed to physical ones", –Polanyi wrote– "has always been fascinating to me because it shows the great value of **inexact** [the present author's emphasis] ideas." Chemistry, Polanyi continued, is a world of ideas expressed by such terms as "relative stability", "affinity", "tendency", "inclination", and "general expectation", as descriptions of behavior.

"There is not a single rule in chemistry which is not qualified by important exceptions", he wrote. Chemists would have been ill-advised, he continued, to heed physicists' counsel to abandon vague methods and to restrict investigations to fields where exact laws pertain. The development of chemistry, wrote Polanyi, "would at that moment have stopped dead."[18] Neither the characterisation of substances nor synthesis of compounds could be achieved by exact methods. Chemistry is an art, which depends on enlarging the investigator's field of awareness, a theme that Polanyi would reiterate in later essays and lectures and in his book *Personal Knowledge* of 1958. At a meeting of the Faraday Society in September 1937, Polanyi introduced these ideas about the merits of the inexact in a defense of his semi-empirical approach in transition-state theory by saying: "Personally I attach no importance at the present stage to a precise numerical agreement between theory and experiments, but I believe that the theory can claim to give a reasonable picture of the mechanism of chemical reactions which would otherwise remain in the dark."[19]

Surprisingly, Polanyi's magnum opus *Personal Knowledge* includes very little that is specifically chemical epistemology or discussion of the relation between physics and chemistry. Instead Polanyi applied his experiences during a long career in physical chemistry and his readings in psychology, anthropology, and philosophy to an examination of the nature of scientific practice and of scientific knowledge in general. He did use the example of isotopes, however, to discuss tacit changes in the meaning of scientific language. In the early 1920s, Polanyi wrote in *Personal Knowledge*, isotopes were defined by their same atomic numbers and their chemical inseparability. Following Harold Urey's 1932 discovery of deuterium, however, the criterion of chemical inseparability was tacitly abandoned as an ironclad rule because hydrogen and deuterium were such notable exceptions.[20] Again, then, we see a distinction made between physics and chemistry on the basis of the universal character of the one, and the exceptional character of the other.

Like Paneth in his lecture on epistemology in 1931, Polanyi compared chemical science to the biological and historical sciences, i.e., to natural history. The chemist's description and understanding of chemical elements and compounds, wrote Polanyi in *Personal Knowledge*, requires the kind of connoisseurship demonstrated in the naturalist's identification of biological specimens and the taxonomist's capacity for "delicate discrimination."[21] Polanyi applied the notion of inexactness to Paneth's problem of the persistence of elementary substances in chemical compounds, by postulating the unspecifiability of higher levels of organisation from knowledge of characteristics belonging to lower levels. He invoked the existence in chemical combinations of emergent properties, an idea that harked back to Aristotle in antiquity and to Pierre Duhem, more recently, in the nineteenth century.[22] "Consider the chemical aspects of matter", wrote Polanyi:

"They are fully determined by atomic physics; yet no Laplacean Mind schooled in quantum mechanics could replace the science of chemistry. For chemistry answers questions regarding the interaction of more or less stable chemical substances, and these questions cannot be raised without experience of the substances and of the practical conditions in which they are handled. A Laplacean knowledge which merely predicts what will happen under *any given* conditions cannot tell us what conditions *should be given*; these conditions are determined by the technical skill and peculiar interests of chemists and hence cannot be worked out on paper. Therefore while quantum mechanics can explain in principle all chemical reactions, it cannot replace, even in principle, our knowledge of chemistry. We may acknowledge this as an incipient separation of two forms of existence."[23]

The notion of emergent properties in complex systems would become more common in philosophy of science in the later decades of the twentieth century.[24] With respect to chemistry, for example, Mario Bunge wrote in 1997 that:

"At first sight chemistry is included in physics because chemical systems would seem to constitute a special class of physical systems. But this impression is mistaken, for what is physical about a chemical systems [sic] is its components rather than the system itself, which possesses emergent (thought explainable) properties in addition to physical properties."[25]

Conclusion

In conclusion, it is to be noted that in their philosophical reflections on the relations between chemistry and physics, there are some striking similarities between the views of the central European physical chemists Fritz Paneth and Michael Polanyi. Their chemical philosophy can be contrasted usefully with the French physical chemist Pierre Duhem, as mentioned earlier. In his philosophy of chemistry and in his philosophy of science more broadly, Duhem was backward-looking, while Paneth and Polanyi were forward-looking. Duhem was an anti-atomist who opposed the use of mechanical models and corpuscular hypotheses in physics and chemistry. Grounding his philosophical views as much in his conservative Catholicism as in his work in thermodynamics and physical science, Duhem taught that physical theory must be purely descriptive and symbolic, leaving statements about reality, such as material reality distinct from sensible appearances, to metaphysics and theology.[26]

Duhem drew upon Aristotelian natural philosophy and medieval Thomism to enhance his understanding of modern physics and thermodynamics. In contrast, Paneth and Polanyi took up the new physics of particles and waves, and of radioactivity and quantum mechanics in their daily practice of chemistry. They admired the new physics, and they knew it well enough to understand differences between current chemical and physical theories and practices. As Paneth said in a talk about inorganic chemistry at a meeting of the British Association in Edinburgh in 1951, "many of the greatest advances in physics have been made on the basis of chemical discoveries . . . . Today there is only one fundamental science of the inorganic world, of which chemistry, physical chemistry, chemical physics, and physics are just different chapters."[27]

Bernadette Bensaude-Vincent has noted the importance of matter theories and chemical concepts in twentieth-century French philosophy of science. With this in mind, Paneth and Polanyi can perhaps be identified more readily not with Duhem's epistemology, but with Gaston Bachelard's 1932 statement of the "pluralisme cohérent de la chimie moderne." [28] No reductionism here, but a recognition of the fruitfulness of the relations between physics and chemistry, as well as their commonalities and differences.

References

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[2] Eric Scerri, "Just How *Ab Initio* Is *Ab Initio* Quantum Chemistry?" *Foundations of Chemistry* 6 (2004): 93-116. Stephen J. Weininger, "The Molecular Structure Conundrum: Can Classical Chemistry Be Reduced to Quantum Chemistry?" *Journal of Chemical* Education 61 (1984): 939-944; Roald Hoffmann, "Nearly Circular Reasoning", *American Scientist* 76 (1988): 182-185; Roald Hoffmann and Pierre Laszlo, "Representation in Chemistry", *Angewandte Chemie*, *International Edition in English* 30 (1991): 1-16; Pierre Laszlo, "Circulation of Concepts", *Foundations of Chemistry* 1 (1999): 225-239.

[3] R. J. Snooks, "Another Scientific Practice Separating Chemistry from Physics: Thought Experiments", *Foundations of Chemistry*, 8 (2006): 255-270.

[4] Eric R. Scerri, "Realism, Reduction, and the 'Intermediate Position,'" in *Of Minds and Molecules: New Philosophical Perspectives on Chemistry*, eds. Nalini Bhushan and Stuart Rosenfeld (Oxford: Oxford University Press, 2000), 51-72, and Scerri, "Some Aspects of the Metaphysics of Chemistry and the Nature of the Elements", *HYLE: International Journal for Philosophy of Chemistry* 11 (2005): 127-145; Fritz Paneth, *Chemistry and Beyond: A Selection*, eds. Herbert

Dingle and G. R. Martin, with the assistance of Eva Paneth (New York: Interscience Publishers, 1964); and Klaus Ruthenberg, "Friedrich Adolf Paneth (1887-1958), *HYLE* 3 (1997): 103-106.

[5] On Polanyi as a "philosophising chemist", Mary Jo Nye, "Michael Polanyi (1891-1976)", *HYLE* 8 (2002): 123-127; and Nye, "Historical Sources of Science-as-Social Practice: Michael Polanyi's Berlin", *Historical Studies in the Physical and Biological Sciences* 37, (2007): 411-436. More generally, William Taussig Scott and Martin X. Moleski, S.J., *Michael Polanyi: Scientist and Philosopher* (Oxford: Oxford University Press, 2005).

[6] F. A. Paneth, "The Epistemological Status of the Chemical Concept of Element", Parts I and II, translated H. R. Paneth [Heinz Post], *British Journal for the Philosophy of Science* 13 (1962): 1-14 and 144-160. Originally in *Schriften der Königsberger Gelehrten Gesellschaft, Naturwissenschaftliche Klasse* 4 (1931). Heinz Paneth changed his last name to Post sometime around 1953. Post was Lecturer in Theoretical Physics and later Head of the Department of History and Philosophy of Science at Chelsea College in the University of London (before it merged with King's College). See Scerri, "Realism, Reduction, and the 'Intermediate Position,'", 67, note 2; and Scerri, "Editorial 1", *Foundations of Chemistry* 1 (1999): 1-5. Also, Harmke Kamminga, Steven French, and Melvin Earles, "Introduction", in *Correspondence, Invariance and Heuristics: Essays in Honour of Heinz Post*, eds. Steven French and Harmke Kamminga (Dordrecht: Kluwer Academic Publishers, 1993), xiii-xxiii.

[7] Ruthenberg, "Friedrich Adolf Paneth;" Keith J. Laidler, *The World of Physical Chemistry* (Oxford: Oxford University Press, 1993) 265-266; and more extensively, H. J. Emeléus, "Friedrich Adolf Paneth. 1887-1958", *B*iographical Memoirs of Fellows of the Royal Society 6 (Nov., 1960): 226-246.

[8] See R. A. Hodgkin and Eugene P. Wigner, "Michael Polanyi, 1891-1976", *Biographical Memoirs of Fellows of the Royal Society* 23 (1977), 421-448. Also, Michael T. Scott, "Michael Polanyi's Creativity in Chemistry", in *Springs of Scientific Creativity* eds. Rutherford Aris, et al. (Minneapolis: University of Minnesota Press, 1983), 279-307; Mary Jo Nye, "At the Boundaries: Michael Polanyi's Work on Surfaces and the Solid State", in *Chemical Sciences in the Twentieth Century,* ed. Carsten Reinhardt, ed. (Berlin: Wiley-VCH, 2001), 246-257; and Mary Jo Nye, "Working Tools for Theoretical Chemistry: Polanyi, Eyring, and Debates over the 'Semi-Empirical Method,'" *Journal of Computational Chemistry* 28, #1 (15 January 2007), 98-108.

[9] Scott and Moleski, *Michael Polanyi*, 64, 123.

[10] Emeléus, "Paneth", 227, 231.

[11] F. A. Paneth and G. von Hevesy, "Zur Frage der isotopen Elemente", *Physikalische Zeitschrift* 15 (1914): 797-805, and Kasimir Fajans, "Zur Frage der isotopen Elemente", *Physikalische Zeitschrift* 15 (1914): 935-940. See Scerri, "Realism, Reduction, and the 'Intermediate Position,'" 65; and Paul van der Vet, "The Debate between F. A. Paneth, G. von Hevesy, and K Fajans on the Concept of Chemical Identity", *Janus: Revue Internationale de l'Histoire des Sciences de la Médecine et de la Technique* 66 (1977): 285-303, esp. 288-298. Note, in contrast to Snooks's argument against thought experiments in chemistry, Van der Vet's description on p. 295 of a thought experiment by Fajans.

[12] F. A. Paneth, "Ueber den Element-und Atombegriff in Chemie und Radiologie", *Zeitschrift für physikalische Chemie* 91 (1916): 171-198 and Kasimir Fajans, in *Jahrbuch der Radioactivität und Elektronik* 24 (1917): 314-352, cited in Scott and Moleski, *Michael Polanyi*, 40. For bibliography of other relevant articles see Emeléus, 244-245. On the decision in 1923 by the International Committee on Chemical Elements, see Francis Aston et al., "Report of the International Committee on Chemical Elements", *Journal of the American Chemical Society* 45 (1932): 867-874.

[13] Paneth, "Epistemological Status", 5-8 (citing Emil Fischer's *Aus meinem Leben* of 1922). Quotation on successes of chemistry, on 6.
[14] Paneth, "Epistemological Status", 151-153; and, on Boyle and Spinoza, 157-158.
[15] Paneth, "Epistmological Status", 155, quoting from Dmitri Mendeleev, *Principles of Chemistry* (1891), 23.
[16] Paneth, "Epistemological Status", 156. On Mendeleev, also Paneth, "Chemical Elements and Primordial Matter: Mendeleeff's View and the Present Position", in *Chemistry and Beyond* ed. Dingle and Martin, 53-72, on 57-58. A translation of "Chemische Elemente und Urmaterie: Mendeleevs Ansicht und der heutige Stanfpunkt", in *Travaux du Congrès Jubilaire Mendéléev* Academy of Sciences of the USSR (Leningrad, 1936).
[17] See Nye, "Working Tools for Theoretical Chemistry", 104-105.
[18] Michael Polanyi, "The Value of the Inexact", reprinted in *Tradition and Discovery* 18, #3 (1992): 35-36.
[19] Michael Polanyi, in "Discussion", *Transactions of the Faraday Society* 33: 28.
[20] On Polanyi's role, Scott and Moleski, *Michael Polanyi*, 38-40. Polanyi, *Personal Knowledge*, 111.
[21] Polanyi, *Personal Knowledge*, 80-81, 351-352.
[22] Pierre Duhem, *Mixture and Chemical Combination and Related Essays*, trans.Paul Needham (Dordrecht: Kluwer, 2002), originally "La notion de mixte: Essai historique et critique", *Revue Philosophique* 1 (December 1900): 69-99 ; 2 (February 1901): 167-197 ; 3 (April 1901): 331-357 ; 4 (June 1901):430-467 ; 6 (October 1901): 730-745. See Bernadette Bensaude-Vincent, "Chemistry in the French Tradition of Philosophy of Science: Duhem, Meyerson, Metzger and Bachelard", *Studies in the History and Philosophy of Science* 36 (2005): 627-648. The idea of emergent properties can be found in John Stuart Mill's discussion in the *System of Logic* of what Mill called heteropathic effects in chemical composition. See Mill's *A System of Logic, Ratiocinative and Inductive: Being a Connected View of the Principles of Evidence and the Methods of Scientific Investigation (*New York: Harper & Brothers, 1860), Book III, Chapter 6, Section 1.
[23] Polanyi, *Personal Knowledge*, 393-394.
[24] Ansgar Beckermann et al., eds. *Emergence or Reduction?* (Berlin: Walter de Gruyter, 1992) and Philip Clayton and Paul Davies, ed. *The Re-Emergence of Emergence* (Oxford: Oxford University Press, 2006).
[25] Mario Bunge, "Is Chemistry a Branch of Physics?" *Zeitschrift für allgemeine Wissenschaftstheorie* 13 (1982): 209-223, quoted in Eric R. Scerri and Lee McIntyre, "The Case for the Philosophy of Chemistry", *Synthese* 111 (1997): 213-232, on 219.
[26] Pierre Duhem, *The Aim and Structure of Physical Theory*, trans from the 2nd French edition Philip Wiener (Princeton : Princeton University Press, 1954 ; 1st publication 1906), 10, 25-27, 95-99; Pierre Duhem, "L'évolution des theories physiques de xviiie siècle jusqu'à nos jours", *Revue des Questions Scientifiques* 40 (1896): 463-499, on 497-498; and Pierre Duhem, *Physique de croyant*, extract from *Annales de Philosophie Chrétienne* (Paris : Bloud et Cie, 1905), 31-34. See Mary Jo Nye, "The Moral Freedom of Man and the Determinism of Nature: The Catholic Synthesis of Science and History in the *Revue des Questions Scientfiques*", *British Journal for the History of Science* 9 (1976): 274-292.
[27] F. A. Paneth, "The Trend of Inorganic and Physical Chemistry since 1850", in *Chemistry and Beyond,* eds. Dingle and Martin, 29-40, on 37-39. This is a paper read to the Chemistry Section of the British Association for the Advancement of Science at Edinburgh on 9 August 1951 and printed in *Advancement of Science*, 8 (1952), 397 ff.
[28] On Bachelard's *Le pluralisme cohérent de la chimie moderne* (Paris : Vrin, 1932), see Bensaude-Vincent, "Chemistry in the French Tradition". 641.